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RESEARCH PAPER RP913

Part of Journal of Research of the National Bureau of Standards, Volume 17, September 1936

COMPARISON OF DATA ON THE IONOSPHERE, SUNSPOTS, AND TERRESTRIAL MAGNETISM *

By Elbert B. Judson

ABSTRACT

Ionosphere data of the National Bureau of Standards from 1930 to 1935 are compared with data on the earth's magnetic field intensity and sunspot numbers. Seasonal variations of F_2 critical frequency and virtual height are compared with sunspot numbers and magnetic activity. Correlation of annual averages of the ionosphere critical frequencies with sunspot numbers is shown. Variations of midnight F_2 critical frequencies are compared with variations of sunspot numbers and magnetic activity.

It has been shown [1] that there are relations between variations in radio field intensities and similar variations in sunspot activity and disturbances in the earth's magnetic field. The dependence of long-distance radio transmission upon the ionosphere is well known, and it is, therefore, of interest to examine the possible relations between ionosphere data and data on sunspot activity and terrestrial magnetism. It is the purpose of this paper to compare ionosphere data obtained at the National Bureau of Standards from 1930 to 1935 with sunspot activity and variations of the earth's magnetic field during the same period.

The theory and method of measurement of ionosphere phenomena have been treated elsewhere.[2 3] There are three principal regions of the ionosphere capable of returning radio waves back to the earth; the E region, about 100 to 120 km in virtual height, the F_1 region, about 200 to 230 km in virtual height, and the F_2 region, about 240 to 500 km in virtual height, depending upon the season and time of day. The presence of the F_1 region is most marked during the summer day. At night the F_1 and F_2 regions combine to form the night F region, as shown in figure 1.

Two important kinds of data are available for each region from ionosphere measurements, namely, the critical frequency or penetration frequency [4] and the virtual height of the region. From the critical frequency the ionization density is calculated.

* A preliminary version of this paper was presented at the Institute of Radio Engineers Convention in Detroit, Mich., July 3, 1935.

[1] G. W. Pickard, *Correlation of radio reception with solar activity and terrestrial magnetism.* Proc. Inst. Radio Engrs. **15**, 83–97 (February 1927); **15**, 749–766 (September 1927). C. N. Anderson, *Notes on the effect of solar disturbances on transatlantic radio transmission.* Proc. Inst. Radio Engrs. **17**, 1528–1535 (September 1929). L. W. Austin, *Comparison between sunspot numbers, intensity of the earth's magnetic field, and strength of radiotelegraphic signals.* J. Wash. Acad. Sci. **20**, 73–74 (1930), and others.

[2] Pedersen, Propagation of Radio Waves. Chapters V and VI, Copenhagen.

[3] S. S. Kirby, L. V. Berkner, and D. M. Stuart. *Studies of the ionosphere and their application to radio transmission.* BS J. Research **12**, 13 (1934) RP632; Proc. Inst. Radio Engrs. **22**, 4 (April 1934). Also references contained therein.

[4] The critical or penetration frequency is defined as the lowest radio frequency of a wave which penetrates the region at normal incidence. The critical frequency of the ordinary ray of the F_1 region is referred to as f^o_{F1}. The critical frequency of the ordinary ray of the F_1 is known as f^o_{F1} and for the extraordinary ray, f^x_{F1}. There is a separation of approximately 800 kc/s between the critical frequency of the ordinary and extraordinary rays in the F regions. The critical frequency of the E region is given as f_E.

The critical frequency of each region has a definite diurnal characteristic variation. The E critical frequency increases rapidly near sunrise and later more slowly to a maximum at noon, decreasing

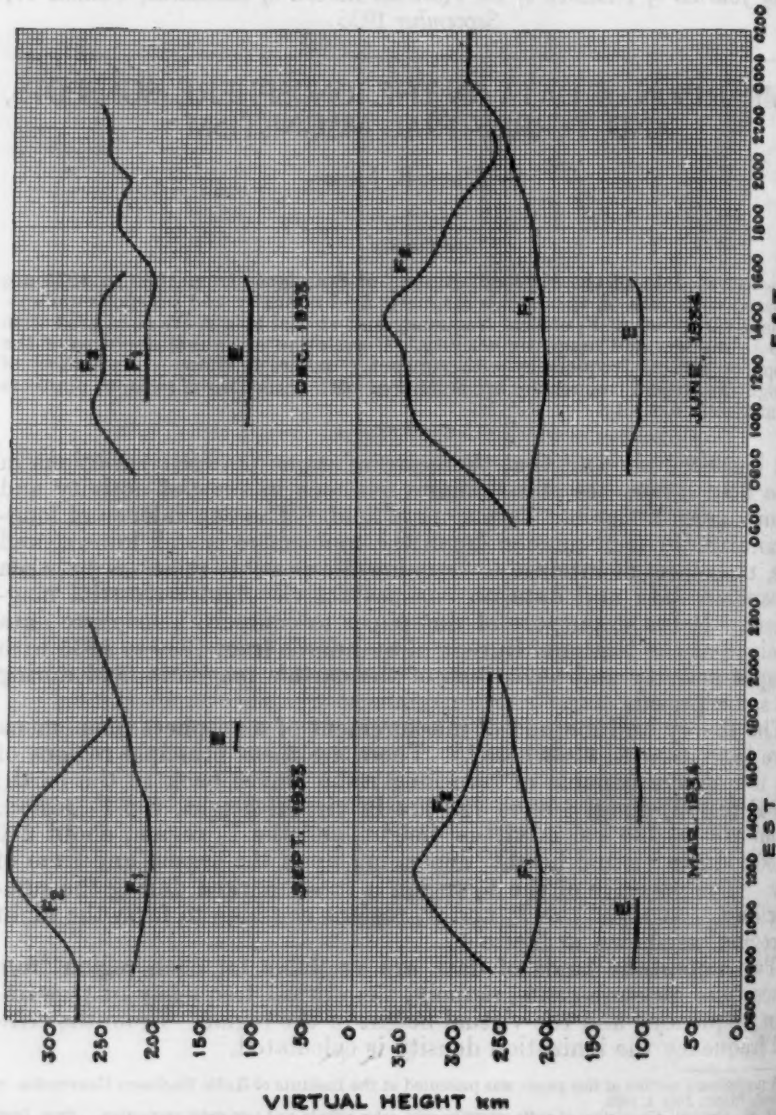

FIGURE 1.—*Average diurnal variation of virtual height of the three ionospheric regions for four seasons.*

slowly during the afternoon and rapidly near sunset. The F_1 region does not form until several hours after sunrise and then f_{F_1} increases slowly to a maximum near noon, decreasing slowly during the afternoon until the F_1 region disappears several hours before sunset. The diurnal curves for f_E and f^0F_1 are given in detail by Gilliland.[5] The

[5] Theodore R. Gilliland, *Multifrequency ionosphere recording and its significance.* J. Research NBS 14, 283–303 (1935) RP769; Proc. Inst. Radio Engrs. 23, 1076–1101 (September 1935).

F_2 critical frequency varies more irregularly than those of the E or F_1 regions. During the winter f_{F_2} is highest just after noon and lowest just before sunrise, while during the summer it is highest just about sunset.

Since there is greater variation in the critical frequency and virtual height of the F_2 region than of the other regions, and since there are data available for this region over a longer period of time, this paper deals mainly with the F_2 region.

Noon critical frequency and virtual height measurements have been made manually once each week in the vicinity of Washington, D. C., since early in 1930. Since May 1933, automatic multifrequency records have been made hourly in the frequency band 2,500 to 4,400 kc/s. Although more complete and accurate data are available for 1933 to 1935, the earlier data give indications of some value.

Figure 2 shows weekly noon values of the F_2 critical frequency extraordinary ray during 1934 and 1935, compared with the sunspot numbers and the magnetic character of the days. The sunspot numbers are the Zürich provisional numbers, while the magnetic character number for each day is that reported by the Cheltenham Magnetic Observatory of the U. S. Coast and Geodetic Survey. The noon (1200 EST) values are not necessarily the maximum points of the diurnal curves. They were selected because the majority of observations during 1930, 1931, and 1932 were taken at or near noon. Here the curve for the year 1934 is placed directly above that of 1935 for comparison. The dotted portion of each curve indicates periods when no data were available. The blank spaces in the critical-frequency curves represent times when no reflections from the F_2 region were returned, or when the F_2 region was masked by a sporadic E layer.[6]

It will be noticed that the critical-frequency values for 1935 were generally higher than for the corresponding time in 1934. Sunspot numbers and magnetic activity were greater in 1935 than in 1934. An examination of the individual days in both years showed no consistent agreement between the curves for the critical frequency and those for the cosmic data. A decrease in critical frequency seemed as likely to happen on quiet days as on magnetically active days. The low values of critical frequency during the summers of 1934 and 1935 and the high values during the winters are indicative of the regular seasonal variation.

Weekly values of noon F_2 critical frequency (extraordinary ray f'_{F_2}) and the virtual height of the F_2 region (for Washington, D. C.) were averaged by months for Sept. 1930 to Dec. 1935, inclusive, and are plotted in figure 3. The F_2 virtual heights plotted were those observed between 4,000 and 5,000 kc/s. The monthly averages of sunspot numbers and the variation of the horizontal component of the earth's magnetic field are also shown in figure 3.

An examination of the critical-frequency and virtual-height curves shows the marked seasonal variation repeating each year and usually having high daytime critical frequencies around February and November of each year. Much lower values of critical frequency are obtained during the summer months. It is of interest to note that when the f'_{F_2} is high the virtual height is low, and vice versa. This condition has also been found to hold for individual days.

[6] Samuel S. Kirby and Elbert B. Judson. *Recent studies of the ionosphere.* J. Research NBS 14, 469-486 (1935) RP780; Proc. Inst. Radio Engrs. 23, 733-751 (July 1935).

The graph of the variation in the horizontal component of the earth's magnetic field is placed directly below that of virtual height and critical frequency to show the similarity in the seasonal variations.

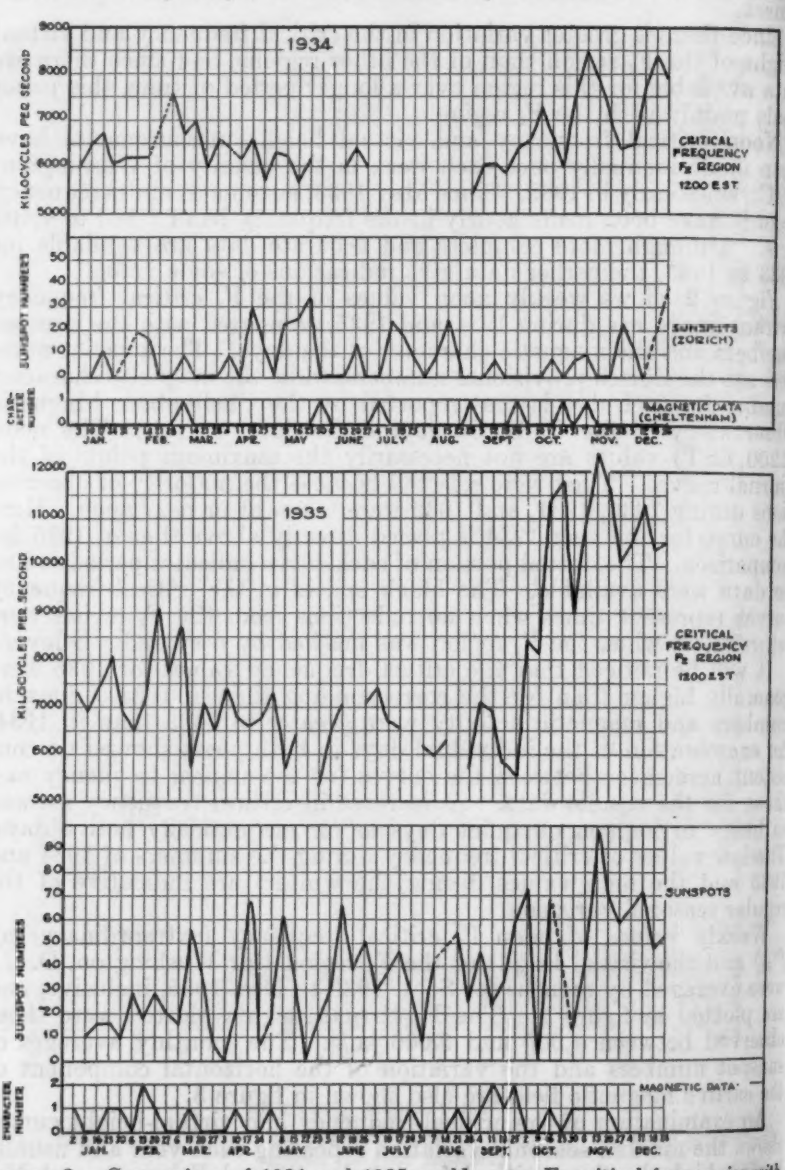
1934
KILOCYCLES PER SECOND
CRITICAL FREQUENCY F_2 REGION 1200 E.S.T.
SUNSPOT NUMBERS
SUNSPOTS (ZURICH)
MAGNETIC DATA (CHELTENHAM)
JAN. FEB. MAR. APR. MAY JUNE JULY AUG. SEPT. OCT. NOV. DEC.
1935
KILOCYCLES PER SECOND
CRITICAL FREQUENCY F_2 REGION 1200 E.S.T.
SUNSPOT NUMBERS
SUNSPOTS
MAGNETIC DATA
JAN. FEB. MAR. APR. MAY JUNE JULY AUG. SEPT. OCT. NOV. DEC.

FIGURE 2.—*Comparison of 1934 and 1935 weekly noon F_2 critical frequencies with sunspot numbers and magnetic activity.*

The seasonal curve of virtual heights follows fairly well the seasonal curve of magnetic disturbances. The critical-frequency curve and the curve for the magnetic variations appear to have an inverse relationship. From these comparisons it could not however be concluded that low critical frequencies regularly occur during short

periods of pronounced magnetic activity. A comparison of the critical-frequency curve with the average sunspot curve shows no certain correlation between the two phenomena for corresponding months. There is, however, a similar general trend when considering the envelopes of the two curves.

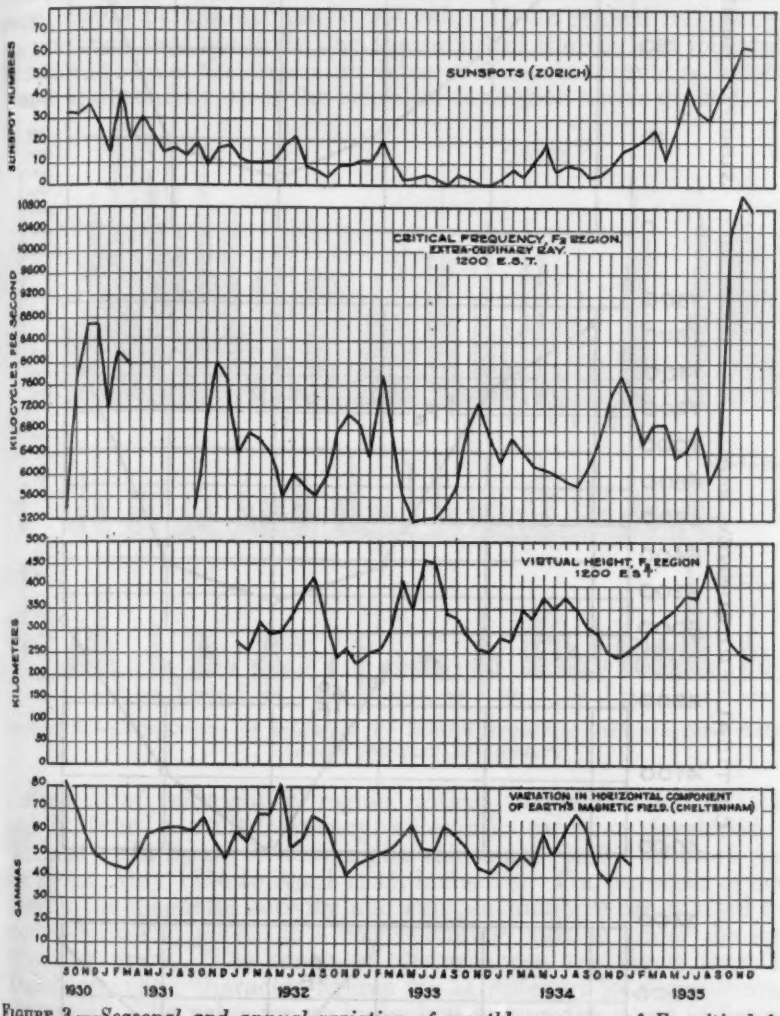

FIGURE 3.—*Seasonal and annual variation of monthly averages of F_2 critical frequency, F_2 virtual height, sunspot numbers, and magnetic activity.*

Annual averages of critical frequencies and sunspots were next considered. In figure 4 the annual averages of sunspot numbers, the critical frequency, extraordinary ray, of the F_2 region, ordinary ray, of the F_1 region and the critical frequency of the E region, are plotted for comparison. The sunspot numbers and F_2 critical-frequency curves are closely related, reaching a minimum in 1933, and rising rapidly together from 1934 to 1935. The F_1 and E region critical frequencies seem to vary similarly, but the trend is much less pro-

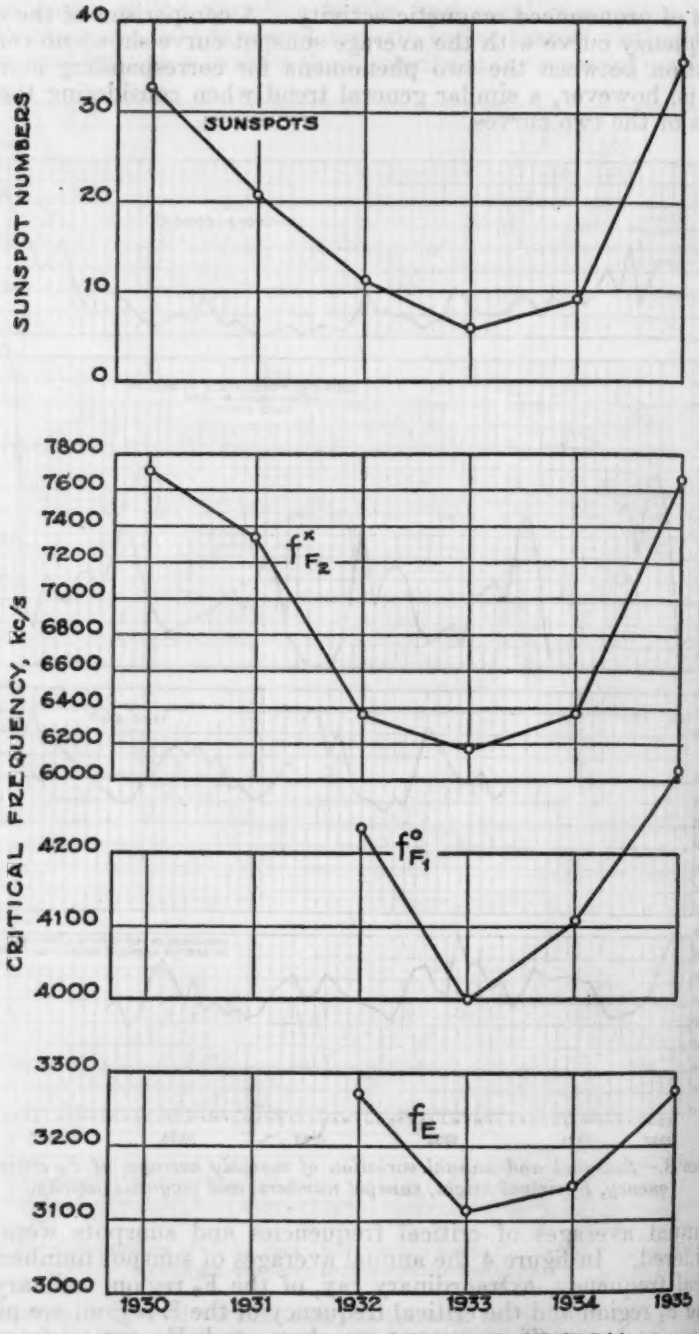

FIGURE 4.—*Annual averages of critical frequencies for the three ionosphere regions compared with the annual average of sunspot numbers.*

nounced (the ordinates in the figure for F_1 and E are different in scale from those of the F_2).

The correlation of these annual averages is suggestive of the possibility of forecasting the most suitable radio frequencies which might be utilized for communication purposes during certain periods of the sunspot cycle. The maximum frequency which would return to earth would be approximately the value of the critical frequency at normal incidence multiplied by the secant of the angle of incidence.[7] For the F_2 region the maximum value of the secant would be between 3 and 4, depending upon the height of the region above ground.

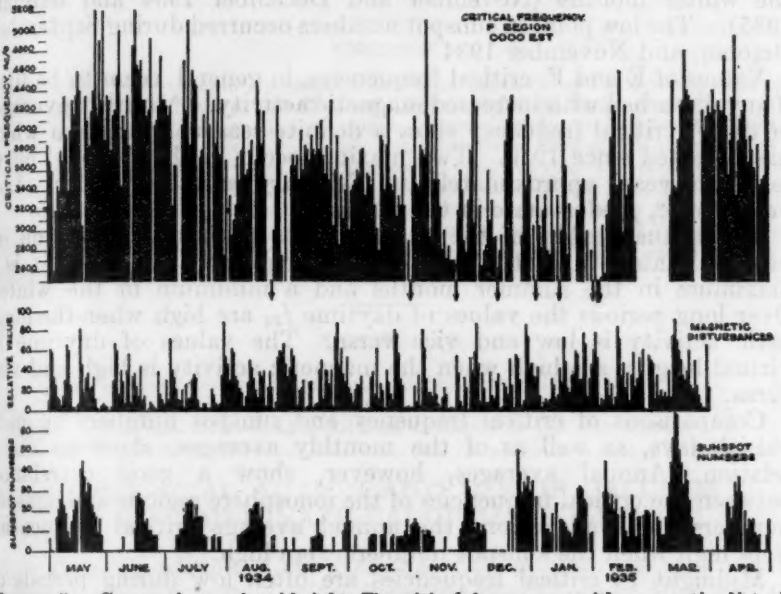

FIGURE 5.—*Comparison of midnight F^2 critical frequency with magnetic disturbances and sunspot numbers.*

Records of midnight F region critical frequencies are obtained nightly from a multifrequency automatic recorder developed by Gilliland.[8] In figure 5. these night values are plotted in block form for 1 year, May 1934 to April 1935, inclusive. For purposes of comparison the magnetic activity and sunspot numbers are plotted in a similar form and placed in a corresponding position under the ionosphere diagram. The magnetic disturbances are taken from the DeBilt magnetic character figures for 44 different locations through the world. The value for an individual day on the curve in figure 5 represents the sum of the DeBilt character figures. The sunspot numbers are the provisional numbers (Zurich) for each day. The F critical frequency shown is for the extraordinary ray. Blank spaces extending to the bottom of the block show that the record was either spoiled or missing. The arrows pointing downward from the bottom of the block show that the critical frequency was below 2,500 kc/s. (2,500 kc/s is the lower limit of frequency of the automatic recorder).

[7] See footnote 3.

[8] T. R. Gilliland, *Note on multi-frequency automatic recorder of ionosphere heights.* BS J. Research 11, 481-486 (1933) RP608; Proc. Inst. Radio Engrs. 22, 236-246 (1934).

Comparison of the critical-frequency diagram with that for magnetic disturbances shows that in quite a number of instances a drop in the critical frequency happens on a night when there is increased magnetic activity. Best agreement appears in the summer months. The highest groups of critical frequencies appear to be associated with minimum groups of magnetic activity.

Sunspot numbers show very little correlation with the critical-frequency curve.

The seasonal variation for midnight critical frequencies for this particular year shows the values high in the summer and lower in the winter months (November and December 1934 and January 1935). The low point in sunspot numbers occurred during September, October, and November 1934.

Values of E and F_1 critical frequencies, in general, seem to be little if any disturbed with increased magnetic activity. Monthly averages of the F_2 critical frequency show a definite seasonal variation which has repeated since 1930. Two maxima occur in the seasonal curve for each year, approximately in February and November. Low values of f_{F_2} predominate in the summer.

The virtual height of the F_2 region has a seasonal variation inversely related to that of the critical frequency. The height is a maximum in the summer months and a minimum in the winter. Over long periods the values of daytime f_{F_2} are high when the magnetic activity is low and vice versa. The values of daytime F_2 virtual heights are high when the magnetic activity is high and vice versa.

Comparisons of critical frequency and sunspot numbers on individual days, as well as of the monthly averages, show no direct relation. Annual averages, however, show a good correlation between the critical frequencies of the ionosphere regions and sunspot numbers. For all regions the annual average critical frequencies were high when the sunspot numbers were high.

Midnight F_2 critical frequencies are often low during periods of high magnetic activity, especially in the summer months; this condition was not found during the winter.

WASHINGTON, July 18, 1936.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP914

Part of Journal of Research of the National Bureau of Standards, Volume 17, September 1936

PREPARATION AND PROPERTIES OF CALCIUM LACTOBIONATE-CALCIUM BROMIDE

By Horace S. Isbell

ABSTRACT

The double salt of calcium lactobionate and calcium bromide, which was prepared for the first time at the National Bureau of Standards, gives promise of becoming an important medicinal agent. According to clinical tests published in foreign journals, its sedative action is almost twice that which corresponds to its bromine content, and when administered in effective quantity it does not cause "bromide rashes" such as frequently develop when alkali bromides are used. The prevalence in the United States of neurasthenia and similar ailments which require sedatives of various types should afford a lucrative market for this salt. The simple process for its manufacture reported in this paper should make it available to all for the alleviation of suffering and distress.

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III. Use of calcium lactobionate-calcium bromide in the manufacture of calcium lactobionate	334

I. MEDICAL ACTION AND USE OF CALCIUM LACTOBIONATE-CALCIUM BROMIDE

In the 1887 edition of the National Dispensatory[1] it was pointed out that calcium bromide "produces the characteristic effects of the bromides more promptly than the analogous compounds, and also induces sleep where they failed to do so." It was also mentioned that calcium bromide is supposedly "peculiarly appropriate for relieving the *insomnia* caused by mental labor or excitement, and the exhausted and irritable states of the nervous system, accompanied by headache, vertigo, insomnia, and extreme mental excitability", and that it "cured epilepsy in very young infants when bromide of potassium failed." In spite of these statements calcium bromide has failed to gain much support from the medical profession, possibly because it is very deliquescent and has a pungent, bitter, disagreeable taste.

In 1927 a double salt of calcium lactobionate and calcium chloride was described in a patent issued to Stoll and Kussmal.[2] At that time the writer was working with C. S. Hudson on the oxidation of aldoses and had on hand some amorphous calcium lactobionate from which he prepared a new crystalline calcium bromide salt analogous to the calcium chloride salt of Stoll and Kussmal. In marked contrast to calcium bromide the new salt is not hygroscopic and may be kept indefinitely without appreciable deterioration. Moreover, it has a

[1] 4th edition, p. 350 (1887).
[2] U. S. Patent 1 648 368 (Nov. 8, 1927).

mild taste which is much less disagreeable than that of the widely used sodium, potassium, and ammonium bromides.

These facts, together with the knowledge that the calcium salts of the sugar acids, as well as calcium bromide, have sedative properties, led the writer to believe that the new salt had sufficient therapeutic value to justify obtaining a public service patent.

The application which was filed and assigned to the United States Government became involved in interference with an application filed by Stoll and Burckhardt. The testimony which was introduced during the interference indicates that subsequent to the preparation of the salt in this country it was prepared by Stoll and Burckhardt in Switzerland and subjected to numerous clinical tests. As has been anticipated, the new salt proved to have valuable therapeutic properties. Administration of the compound in 67 cases is reported by W. Winterseel [3] in an article entitled Kombinierte Brom-Calciumbehandlung mit Calcibromat (Sandoz); and 47 cases are given by E. Blum [4] in an article entitled Klinische Erfahrungen ueber eigenartige synergistische Brom-Kalzium-Wirkung in der Neurologie.

The clinical tests described in these articles indicate that the compound is useful in the treatment of epilepsy, hyperthyroidism, neurasthenia, nervous heart, and other similar ailments. Of particular importance, however, is the fact that the sedative action is much greater than one might anticipate from its bromide content. Thus, it is possible to obtain good results without using sufficient bromide to cause "bromide rashes"; and it is reported that in cases which had been previously treated with "triple bromide" and had developed rashes, these cleared up when calcium lactobionate-calcium bromide was used in place of the triple bromide. These promising results should stimulate interest and clinical investigations of the use of the compound in this country.

II. PREPARATION OF CALCIUM LACTOBIONATE-CALCIUM BROMIDE

Although the simplest method for the preparation of calcium lactobionate-calcium bromide consists in oxidizing lactose with bromine water in the presence of calcium carbonate. followed by crystallization of the double salt from the resulting solution, this method is not economical because only half of the bromine is converted into the double salt. This objectionable feature can be eliminated by combining the bromine oxidation with the electrolytic oxidation [5] which was worked out at the National Bureau of Standards. The procedure is essentially the same as in the manufacture of calcium gluconate,[6] except that one equivalent of bromine is added and 1 faraday of electricity is used for each equivalent of lactose. If desired the cells can be operated in continuous manner, in which case lactose, calcium carbonate, and bromine are added, while calcium lactobionate-calcium bromide is crystallized from the electrolyzed solution. In

[3] Medizinische Klinik, no. 7, p. 236. (Published by Urban and Schwarzenberg, Berlin, 1934.)
[4] Schweiz. med. Wochschr. 63, 446 (1933).
[5] Isbell, U. S. Patent 1976731 (Oct. 16, 1934).
[6] Isbell, Frush, and Bates, BS J. Research 8, 571 (1932) RP436.

small-scale operations it is generally more convenient to add the lactose, bromine, and calcium carbonate in batches rather than continuously and to separate the product from time to time.

To avoid the handling of bromine the process can be conducted equally satisfactorily by adding calcium bromide in place of bromine, and by using 2 faradays of electricity. For commercial use, however, bromine is preferable because it is cheaper.

The following procedure has been found to give consistently satisfactory results: 1 kg of precipitated calcium carbonate and 3.6 kg of lactose (hydrate) dissolved in 10 liters of water are placed in a 20-liter crock equipped with a mechanical stirrer and 8 graphite electrodes 3 dm long and 2.3 cm in diameter. While the solution is stirred vigorously, 0.8 kg of bromine is added. Considerable foaming occurs which can be controlled by adding a few milliliters of *n*-butyl or of hexyl alcohol. After the bromine has been added and the evolution of carbon dioxide has subsided, a direct current of 10 amperes is passed through the solution, using alternate electrodes as anodes and cathodes. When the electrodes are immersed 2 dm in the solution, 6 volts are required and the current density is about 1.7 amp/dm^2 of anode surface. The current density may be varied over a wide range without materially reducing the efficiency. After about 28 hours when all of the sugar has been oxidized the electric current is stopped, but stirring is continued until the evolution of carbon dioxide ceases, in order that any lactobionic lactone may be converted into calcium lactobionate. After filtration the electrolyzed solution is concentrated under reduced pressure to a sirup from which nearly pure calcium lactobionate-calcium bromide crystallizes. The crystals can be grown in the evaporating pan while concentration is taking place, in a manner similar to the "graining" of sugar. The resulting crystalline product is separated from the mother liquor by means of a centrifugal machine and washed with a high-purity calcium lactobionate-calcium bromide sirup. The mother liquors are ordinarily returned to the electrolytic cell and worked up with the following batch. Yields of over 90 percent are usually obtained.

If desired the product can be purified by dissolving it in hot water and adding several volumes of alcohol, whereupon the salt crystallizes in good yield. But usually it is preferable to crystallize the product from hot water in the following manner: Three parts of the salt are dissolved in two parts of boiling water. A small quantity of decolorizing carbon is added and the solution is filtered and seeded with powdered crystalline calcium lactobionate-calcium bromide. By constant agitation and slow cooling large crystals are obtained which are collected on a filter and washed, first with a small quantity of water saturated with calcium lactobionate-calcium bromide, and finally with aqueous alcohol containing approximately equal volumes of alcohol and water. The product after drying at 50° C corresponds to the following analysis: Calculated for $Ca(C_{12}H_{21}O_{12})_2\ CaBr_2.6H_2O$: Ca, 7.54; Br, 15.04. *Found:* Ca, 7.57; Br, 14.95. An aqueous solution containing 7.3 g per 100 ml gives $[\alpha]_D^{20}=+18.7$. A saturated solution of the hydrated salt at 20° C contains 31.5 percent, by weight, and has a density of 1.183 g per milliliter. It crystallizes in hexagonal prisms which have six rectangular faces.

III. USE OF CALCIUM LACTOBIONATE-CALCIUM BROMIDE IN THE MANUFACTURE OF CALCIUM LACTOBIONATE

Because calcium lactobionate crystallizes in hair-like crystals[7] which are difficult to separate from the mother liquor, it is necessary to use an intermediate salt for separating it from the unoxidized sugar and other impurities.

In their process for the preparation of calcium lactobionate by the electrolytic oxidation of lactose, Isbell and Frush [8] employed the basic calcium salt previously prepared by Hudson and Isbell.[9] The use of this basic salt is objectionable because the accompanying strongly alkaline solution causes severe decomposition of any unoxidized

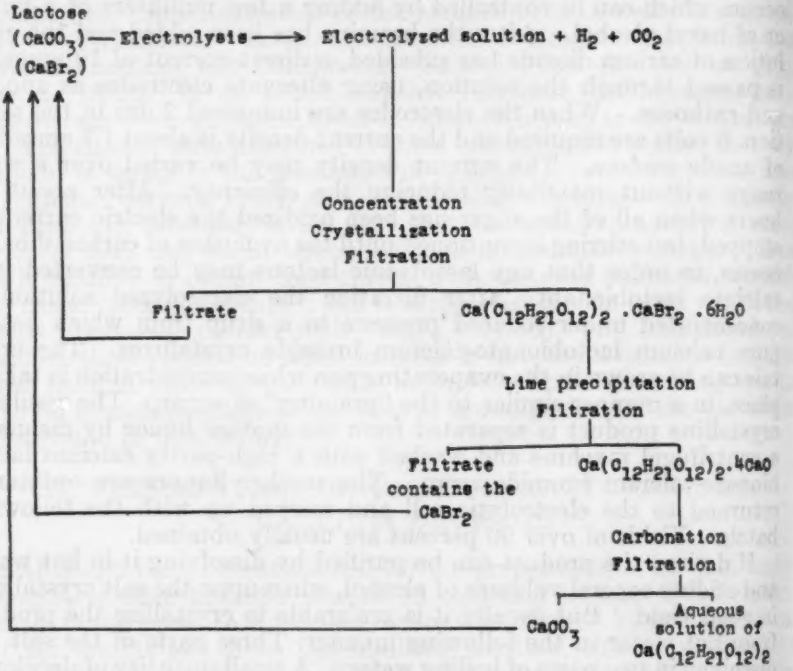

FIGURE 1.

sugar, and thus prevents the satisfactory operation of a continuous process such as that employed in the manufacture of calcium gluconate.[10] By using the calcium bromide double salt in conjunction with the basic calcium salt, the action of alkali on any unoxidized sugar is avoided and the method of manufacture of calcium lactobionate thereby improved.

Equivalent quantities of lactose, calcium carbonate, and calcium bromide are placed in the electrolytic cell and the oxidation is conducted as in the manufacture of calcium gluconate. From time to time crops of crystalline calcium lactobionate-calcium bromide are separated and treated with hydrated lime to give basic calcium

[7] Isbell, BS J. Research **11**, 713 (1933) RP618.
[8] BS J. Research **6**, 1145 (1931) RP328.
[9] BS J. Research **3**, 59 (1929) RP82.
[10] Isbell, Frush, and Bates, BS J. Research **8**, 571 (1932) RP436.

lactobionate and calcium bromide. After separating the basic calcium lactobionate by filtration, the filtrate containing calcium bromide is returned to the electrolytic cell, together with additional lactose and calcium carbonate, and the process continued.

The basic calcium lactobionate is converted into the normal salt by carbonation, giving as a byproduct calcium carbonate, a part of which can be returned to the electrolytic cell. As may be seen from the diagram, lactose and lime are the only raw materials consumed. There is some loss of bromine and occasionally the electrolyte becomes foul and must be discarded and the bromide reclaimed.

The essential features of the process outlined above have been covered by U. S. Patent 1 980 996, which is assigned to the Government of the United States.[11] Figure 1 illustrates the continuity of the various steps in the process.

[11] Anyone desiring to use either patent 1 980 996 or 1 976 731 should make application to the Secretary of Commerce for a license.

WASHINGTON, September 3, 1936

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP915

Part of Journal of Research of the National Bureau of Standards, Volume 17, September 1936

EMPIRICAL RELATION BETWEEN THE ATOMIC DIMENSIONS AND THE MELTING AND SUBLIMATION POINTS OF THE NOBLE GASES, HALOGENS, AND ELEMENTS OF THE SULPHUR GROUP

By D. H. Brauns

ABSTRACT

In comparing the melting points of the noble gases, halogens, and elements of the sulphur group the author found that those elements of these groups which have analogous differences in atomic structure show an apparent relationship between their melting points and their atomic dimensions, the differences in the melting points being proportional to the differences between the corresponding atomic radii. Further, it was found that for these elements with analogous differences in atomic structure an apparent proportionality exists between the differences in the atomic radii and the differences in the sublimation points at low pressure.

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I. INTRODUCTION

A relationship between optical rotation and atomic dimension has been previously pointed out and is being studied by the writer.[1] Other relations such as chemical affinity in which atomic dimensions seem to play a role were also observed.[2] Since halogen *derivatives* were used for the investigation of these relations it seemed desirable to look for any apparent relationship between the physical characteristics of the halogen *elements* and their atomic dimensions and to extend the study to other available groups of elements. The present paper embodies the results of this study.

[1] BS J. Research 7, 573 (1931) RP358; J. Am. Chem. Soc. 56, 1421 (1934).
[2] J. Am. Chem. Soc. 45, 2385 (1923).

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II. RELATIONSHIP BETWEEN ATOMIC RADII AND MELTING POINTS FOR ELEMENTS WITH ANALOGOUS DIFFERENCES IN ATOMIC STRUCTURE

In studying the relationship between atomic radii and melting points, comparisons have been made, using the noble gases, halogens, and elements of the sulphur group. Hydrogen has been included in the group of the halogens as it often behaves in a manner analogous to that of the halogens both as free elements and in organic compounds.[3] The data are given in table 1.

It will be observed from table 1:

(1) That for the heavier elements of the noble gases, of the halogens, and of the sulphur group (A, Kr, Xe), (Cl, Br, I), and (S, Se, Te) the ratio $\frac{\Delta ar}{\Delta mp} \times 10^{-2}$ agrees well since (A, Kr, Xe) show 0.46 and 0.46; further (Cl, Br, I) show 0.14 and 0.15; and finally (S, Se, Te) 0.11 and 0.10.

(2) Also that the lighter elements of the noble gases (He, Ne, A) show an agreement 0.78 and 0.71, and the lighter elements of the halogen group (H, F, Cl) show 0.33 and 0.34. However, the ratio for (He, Ne, A), 0.71, differs from the ratio for the heavier elements (A, Kr, Xe), 0.46. This ratio is still smaller for the lighter halogens (H, F, Cl), 0.33, decreasing further for the heavier halogens, 0.14, and still further for the sulphur elements to 0.11. The less accurate agreement for (He, Ne, A) may be due to the nonsolidification of He under its own vapor pressure. The above relationship in the cases where it is found to hold can be correlated to and explained by the structure of the atoms. Comparing the structure of atoms built up in successive electron shells,[4] the writer observed that the noble gases (which will serve as the basis for all comparisons) can be arranged into two groups, as shown in table 2.

	Melting Points	Atomic Radii in A [a]	Ratio $\frac{\Delta ar}{\Delta mp} \times 10^{-2}$
Noble gases			
He	(-273.1)	0.93	(0.78)
Ne	-248.7	1.12	.71
A	-189.3	1.54	.46
Kr	-157	1.69	.46
Xe	-112	1.90	
Halogens			
H	-259.1	0.53	.33
F	-217	0.67	.34
Cl	-102.5	1.05-1.07	.14
Br	- 7.3	1.19	.15
I	114.1	1.36-1.40	
Elements of the sulphur group			
O	-218.4	0.60	.13
S	112.8	1.02-1.04	.11
Se	220.2	1.13-1.17	.10
Te	453	1.33-1.43	

(References to the data used are given at the end of this article, pages 343-345)

TABLE 1.—*Comparison of melting-point differences of the noble gases, halogens, and elements of the sulphur group with atomic-radii differences*

[3] Van Arkel and De Boer, Z. Physik 41, 27 (1927).
[4] Kramers and Holst, De Bouw der Atomen (Amsterdam, ed. 2, p. 169, 1930).

Group (He, Ne, A).—Ne differs from He, and A from Ne in an identical manner by the presence of 8 electrons in groups of 2 and 6 in the next energy level.

Group (A, Kr, Xe).—Kr differs from A, and Xe from Kr in an identical manner by the presence of an energy level of 18 electrons in groups of 2, 6, and 10 inserted below the outer energy level.

Energy level or main quantum number	K	L		M			N				O	
	1 Quantum	2 Quanta		3 Quanta			4 Quanta				5 Quanta	
Noble Gases												
He	2											
Ne	2	2	6									
A	2	2	6	2	6							
A	2	2	6	2	6							
Kr	2	2	6	2	6	10	2	6				
Xe	2	2	6	2	6	10	2	6	10		2	6
Halogens												
H	1											
F	2	2	5									
Cl	2	2	6	2	5							
Cl	2	2	6	2	5							
Br	2	2	6	2	6	10	2	5				
I	2	2	6	2	6	10	2	6	10		2	5
Elements of the Sulphur Group												
O	2	2	4									
S	2	2	6	2	4							
S	2	2	6	2	4							
Se	2	2	6	2	6	10	2	4				
Te	2	2	6	2	6	10	2	6	10		2	4

TABLE 2.—*Groupings of electrons in the atoms.*

By omitting one outer electron, group (He, Ne, A) yields group (H, F, Cl) and by omitting one and two outer electrons, respectively, group (A, Kr, Xe) yields the groups (Cl, Br, I) and (S, Se, Te), respectively, which show the same melting-point relation.

The group of the alkali and earth alkali metals do not show any regularities, which is probably connected with the exceptional elliptical comet orbit of their outer electrons. Evidence is thus obtained that the noble gases, halogens, and elements of the sulphur group can be divided into two groups based on analogous difference in electronic structure, which is paralleled by an identical division based on the ratio of the successive differences in atomic radii to the respective differences in melting points $\left(\frac{\Delta ar}{\Delta mp} \times 10^{-2}\right)$.

III. RELATIONSHIP BETWEEN ATOMIC RADII AND SUBLIMATION POINTS AT LOW PRESSURE FOR THE SAME ELEMENTS

It may be expected from the above discussed melting-point-atomic-dimension relation and the well known rule of Ramsay and Young that atomic-dimension differences may be related in the same simple way to temperature differences for the above sets of elements for any definite pressure at which two phases are in equilibrium.

This rule of Ramsay and Young [5] states that for closely related substances the ratio of the absolute temperatures corresponding to equal vapor pressures of the liquid is constant. The authors derived this rule from the vapor pressures of ethyl chloride, ethyl bromide, and ethyl iodide, and also for chloro and bromo benzene for which vapor pressure data for the liquid phases were available. By a simple mathematical deduction the rule of Ramsay and Young may also be stated as follows: The ratio of phase-equilibrium temperature differences for a group of closely related substances is constant at all pressures. However, by making a graphical comparison of p–t relations for the above mentioned groups of elements, (He, Ne, A), (A, Kr, Xe), (Cl, Br, I), etc. (using for each group the same axes of coordinates by which temperature differences for a certain pressure can be easily read on lines parallel to the X axis) two observations were made which cannot be derived by the above considerations:

(Br-Cl):(I-Br)

Pressure in mm Hg	Ratio of phase-equilibrium temperature differences	Ratio of atomic-dimension differences
Solid phases		
0.0025	17.1 : 22.0	17.1 : 21.8 (from melting-point relation)
0.0090	17.1 : 22.3	
0.030	17.1 : 22.2	17.1 : 21.4 (from optical-rotation relation)
0.25	17.1 : 23.2	
8	17.1 : 22.6	
Different phases		
20	17.1 : 23.2	
60	17.1 : 23.3	
80	17.1 : 23.2	
Liquid phases		
110	17.1 : 23.3	
180	17.1 : 23.0	
370	17.1 : 23.3	
465	17.1 : 23.2	

TABLE 3.

(1) The ratio of phase-equilibrium temperature differences for these groups of elements is not quite constant but tends to approach a value equal to the ratio of the respective atomic-dimension differences only at the lowest pressures.

(2) In this graphical comparison the melting points for a group of elements are situated on a straight line.

The most reliable data for checking the first observation are those for the (Cl, Br, I) group.[6] The data are given in table 3.

[5] Phil. Mag. **29**, 530 (1885); also **21**, 33 (1886).

[6] Also for the group (A, Kr, Xe) it was found that the ratio of the temperature differences (Kr–A): (Xe–Kr at the lowest pressure measured (22 mm) is 15:21.2, agreeing very well with the atomic-dimension differences (15:21), and further that the deviation becomes more pronounced the higher the pressure. That this deviation for higher pressures for the group (A, Kr, Xe) is in the opposite direction to the deviation for (He, Ne, A) and also for the group (Cl, Br, I) could not be explained (see also footnote 8). The temperature relationship for the group (He, Ne, A) does not show a close agreement at the lowest pressure measured. This ratio is 19:49.9 at 22 mm, whereas the ratio for the atomic-dimension differences is 19:42. It is obvious that in this relationship as in the melting-point relation the behavior of He is not strictly comparable with that of Ne and A. However, for 25.8 kg/cm² the melting point relation for these elements is 19:46.5; for 145.3 kg, 19:50.5; and for 1,800 kg, 19:59, showing the tendency to diminish to the atomic-dimension ratio at ordinary pressure.

The ratio for the atomic-dimension differences (Br–Cl):(I–Br), 17.1:21.4, was obtained by the author from the investigation of optical rotation and atomic dimension. A discussion of the available data, including the Goldschmidt values was also given.[7,8] It will be seen that this ratio agrees very closely with that calculated from the melting-point relation (table 1) and also with that for the phase-equilibrium temperature relation for the lowest pressure determined (0.0025 mm, table 3). Above 0.25-mm pressure the ratio deviates appreciably.

From the second observation that the melting points of Cl, Br, and I are situated on a straight line in the graphical comparison a deduction can be made. If a line be drawn through the melting point of chlorine parallel to the X axis, and lines perpendicular thereto through the melting points of bromine and iodine, similar triangles are formed thereby. If the melting-point-atomic dimension ratio holds for these elements, as suggested above, it follows that the distance between the melting points on the straight line will have the same ratio as the respective atomic-dimension differences. The same peculiarity may hold for (S, Se, Te), although experimental data are conflicting and are complicated by the presence of allotropic forms. The data of different investigators for the vapor pressures at the melting points for Kr and Xe disagree to such an extent[9] that the group (A, Kr, Xe) cannot be tested for this peculiarity (see fig. 1). Its existence cannot be determined for (He, Ne, A) as He probably cannot be obtained in the solid phase under its own vapor pressure. In figure 3 an application of this observation was made, indicating that ordinary hydrogen belongs in the series with F and Cl and not deuterium. However, the melting point of F has not been recorded with sufficient accuracy for checking the regularity.

IV. CONCLUSIONS

From the discussion given above it is clear that there is evidence that existing data indicate relationships between melting points, and also phase-equilibrium temperatures at low pressure, and atomic dimensions for elements with analogous differences in atomic structure.

The relationships indicated are especially interesting owing to the fact that melting points and phase-equilibrium temperatures at low pressures are not directly atomic properties but are properly included in the phase theory.

The author expresses his thanks to Frederick Bates for his interest and suggestions.

V. PRESSURE-TEMPERATURE CURVES

(Figures 1, 2, and 3)

NOTE.—The values used for calculating the ratios (Ne–He): (A–Ne); (Kr–A): (Xe–Kr); (Br–Cl): (I–Br); and (F–H): (Cl–F) were obtained from the original accurately constructed large-scale figures plotted on millimeter cross-section paper, of which figures 1 and 2 are reproductions.

[7] See footnote 1, p. 337.

[8] J. Am. Chem. Soc. 47, 1280 (1925). In this connection it is noteworthy that the relationship between optical rotation and atomic dimension holds not only for Cl, Br, and I derivatives but also includes the F and most probably also the H derivative.

[9] Recent investigations of vapor pressures of solid and liquid Kr by Justi (see literature references at end of paper) agree with the results of Peters and Weil, whereas the results of Keesom, Mazur, and Melhuizen on vapor pressures of solid Kr disagree notably for the vapor pressure at the melting point.

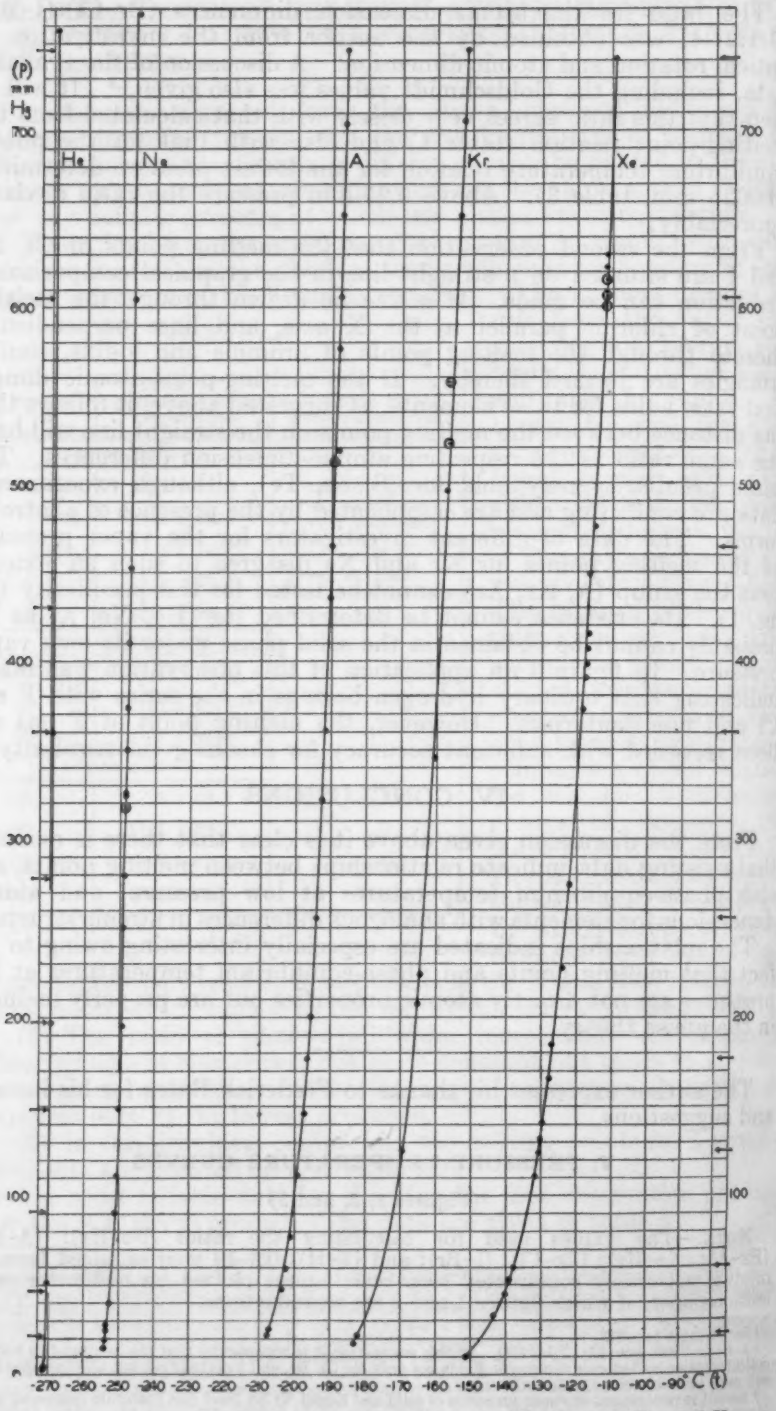

FIGURE 1.—*Pressure-temperature curves for* He, Ne, A, Kr, *and* Xe.

KEY (figs. 1, 2, and 3):
•Experimental data taken from the literature for constructing the p–t curves.
⊙Melting points. (For references see tables 1, 2, and 3 and list of the literatures on page 343–345 of this paper.
→Pressures at which measurements were made.

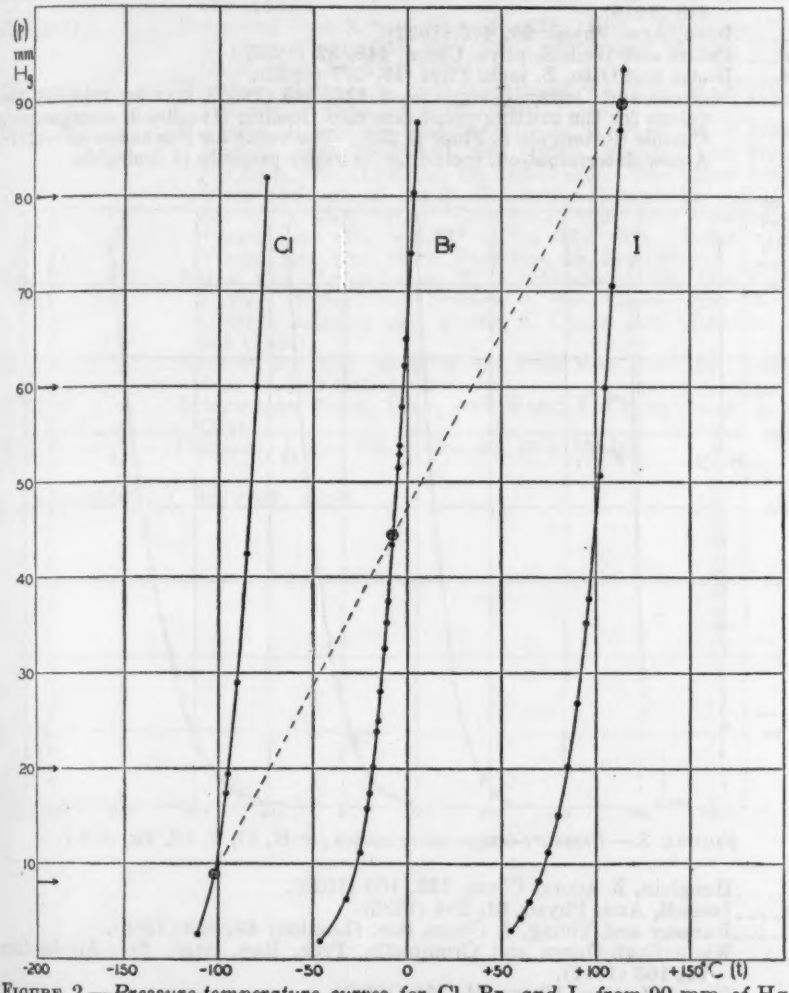

FIGURE 2.—*Pressure-temperature curves for* Cl, Br, *and* I, *from* 90 mm *of* Hg *to* 475 mm *of* Hg.

VI. LITERATURE FOR VALUES OF ATOMIC DIMENSIONS AND MELTING POINTS

1. ATOMIC DIMENSIONS

The values of Wherry (Am. Mineralogist **14,** 54; 1929) of the neutral (not ionized) atoms are given. These values are compiled from Goldschmidt (Die Gesetze der Krystallochemie, Skr. Norske Vidensk. Akad. Oslo **I,** Mat. Nat. Kl. No. 2, 117; 1926) and Pauling (J. Am. Chem. Soc. **49,** 765; 1927). The atomic radius of $H=(0.5285 \pm 0.004)\times 10^{-8}$ (Birge, Phys. Rev., Supp. 1; 1929). Jeans' Dynamic Theory of Gases (p. 152, 1916) gives H_2=atomic hydrogen= 0.502A to 0.63A; Bergmann and Engel (Z. phys. Chem. **13,** 247) for the radius of hydrogen in the vapor state, 0.48A.

2. MELTING POINTS

The value, as deemed most probable, is given, not an average of the most recent values.

He....Keesom, Proc. Roy. Acad. Amsterdam **29,** 1136 (1926).
Ne....Kamerlingh-Onnes and Crommelin, Proc. Roy. Acad. Sci. Amsterdam **18,** 518 (1916).
A.....Born, Ann. Physik **69,** 473 (1922).
Kr....Peters and Weil, Z. phys. Chem. **148,** 32 (1930).
Xe....Heuse and Otto, Z. tech. Phys. **13,** 277 (1932).
F.....Moissan and Dewar, Compt. rend. **136,** 643 (1903), give by mistake two values for the melting point (see also Gmelin, Handbuch anorganische Chemie System no. 5, Fluor p. 22). The value for F is taken as −217°. A new determination, including its vapor pressure is desirable.

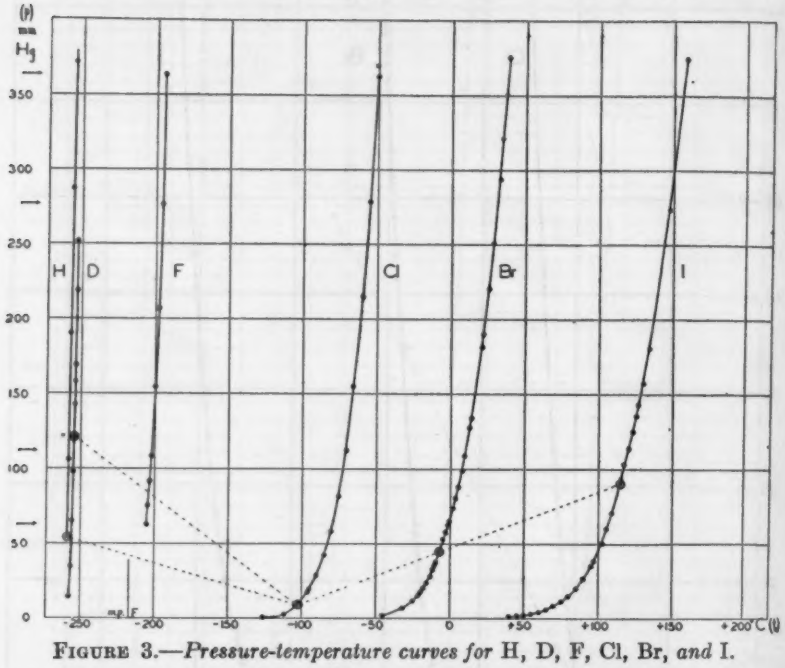

FIGURE 3.—*Pressure-temperature curves for* H, D, F, Cl, Br, *and* I.

Cl.....Henglein, Z. anorg. Chem. **123,** 160 (1923).
Br.....Isnardi, Ann. Physik **61,** 264 (1920).
I.....Ramsay and Young, J. Chem. Soc. (London) **49,** 453 (1886).
O.....Kamerlingh-Onnes and Crommelin, Proc. Roy. Acad. Sci. Amsterdam **14,** 163 (1911).
S.....Kruyt, Z. phys. Chem. **64,** 561 (1908).
Se.....Berger, Z. anorg. Chem. 85, 114 (1914).
Te....Damiens, Ann. chim. phys. [9] **19,** 44 (1923).

VII. LITERATURE FOR DATA ON p–t AND MELTING-POINT CURVES

He (*p–t*).....Kamerlingh-Onnes and Weber, Proc. Roy. Acad. Sci. Amsterdam **18,** 505 (1915).
He (mp curve)...Keesom, Proc. Roy. Acad. Sci. Amsterdam, **29,** 1136 (1926). Simon, Edwards, and Ruhemann, Z. Elektrochem. **35,** 618 (1929). See also note and formula, Z. phys. Chem. [B] **6,** 338 (1929).
Ne (*p–t*).....Crommelin and Gibson, Proc. Acad. Sci. Amsterdam **30,** 364 (1927).
Ne (mp curve)...Simon, Edwards, and Ruhemann, Z. phys. Chem. [B] **6,** 331 (1929).

A (p–t)---------Born, Ann. Physik **69,** 473 (1922).
A (mp curves)---Simon, Edwards, and Ruhemann, Z. phys. Chem. [B] **6,** 331 (1929).
Kr (p–t)---------Peters and Weil, Z. phys. Chem. **148,** 32 (1930). Justi, Phys. Z. **36,** 571 (1935). Keesom, Mazur, Meihuizen Physica **2,** 669 (1935).
Xe (p–t)---------Heuse and Otto, Z. tech. Phys. **13,** 277 (1932). Peters and Weil, Z. phys. Chem. **148,** 32 (1930). Allen and Moore, J. Am. Chem. Soc. **53,** 2522 (1931).
Cl (p–t)---------Henglein, Rosenberg, and Muchlinski, Z. Phys. **11,** 1 (1922) Pellaton, J. chim. phys. **13,** 440 (1915).
Br (p–t)---------Henglein, Rosenberg, and Muchlinski, Z. Phys. **11,** 1 (1922). Isnardi, Ann. Physik **61,** 264 (1920). Ramsay and Young, J. Chem. Soc. (London) **49,** 453 (1886). The value +0.31° C for 65.0 mm of Hg (p. 456, series I) must be −0.31° C See on p. 455: −0.31° C at 65.25 mm; also Scheffer and Voogd, loc. cit., −0.42° C for 64.3 mm. Scheffer and Voogd, Rec. trav. chim. Pays Bas, **45,** 214 (1926).
I (p–t)---------Haber and Kerschbaum, Z. Elektrochem. **20,** 302 (1914). Baxter, Hickey, and Holmes, J. Am. Chem. Soc. **29,** 127 (1907). Ramsay and Young, J. Chem. Soc. (London) **49,** 453 (1886).
H (p–t)---------Keesom, Byl, and van der Horst, Proc. Roy. Acad. Sci. Amsterdam **34,** 223 (1931).
D (p–t)---------Brickwedde, Scott, Urey, and Wahl, J. Chem. Phys. **2,** 456 (1934).
F (p–t)---------Claussen, J. Am. Chem. Soc. **56,** 614 (1934).

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THE FRENCH SUGAR SCALE

By Frederick Bates and Francis P. Phelps

ABSTRACT

Two different saccharimeter scales are in use today, and although each purports to give the correct percentage of sucrose in a given sample, there is an outstanding difference between the two of approximately 0.1 percent. The industrial importance of the commodity sucrose and its associated products in international trade requires that this difference be eliminated.

A research into the history of the French Sugar Scale and its normal weight discloses the fact that the value of this constant now in official use was originally adopted upon evidence which at the present day would be considered insufficient and that although the two subsequent outstanding experimental redeterminations of this constant gave results somewhat smaller than the official value, those results were considered at the time to be ample confirmation of the then accepted value. A calculation from modern data shows that the French normal weight required to bring the International Sugar Scale and the French Sugar Scale into agreement is exactly that actually obtained by the older French investigators whose work is mentioned above.

Two markedly different saccharimeter scales are in use today, each purporting to give the correct percentage of sucrose in a sample. They are the French Scale and the International Sugar Scale. The former is used largely in France and the French Colonies; the latter is used generally throughout the world. The International Sugar Scale is the official scale of the International Commission for Uniform Methods of Sugar Analysis and was adopted at the eighth session of the Commission in 1932, at Amsterdam. Obviously any saccharimeter scale is, by definition, a basis on which the standardization of the saccharimeter may be brought about. In any consideration of the saccharimeter scale it is essential that there be kept clearly in mind the differentiation between mere definition of the scale and the numerical values of the constants upon which its correctness depends. The confusion which has always existed with regard to saccharimeter scales may be correctly attributed to the inaccurate determination of these constants.

Probably no industrial commodity is so widely utilized in international trade as sucrose and its associated products. Therefore, it is of great importance that there be but one sugar scale, that is, one basis of standardization of saccharimeters in use throughout the world. Such a consummation must ultimately be brought about in view of the importance of the matter to international trade and especially because of the necessity of reporting the results of research workers in unmistakable values. Until this can be done, and under present conditions it is therefore of special importance, insofar as the inherent characteristics of the French and the International Sugar Scales will permit, that the two scales give results that are in agreement within

the experimental error with which saccharimeter measurements can be made. It is fundamental that tests of a sample of sucrose should show an identical sucrose content regardless of the scale used.

After a number of changes had been made in the normal weight for the French Scale, the value 16.29 g, weighed in air with brass weights, was officially adopted in 1896, and has been the official value ever since. Because of the uncertainty which existed regarding the correctness of the value 16.29 g, two subsequent redeterminations of the value of the normal weight were carried out by French investigators. The reported values were considered "sufficiently close" to the then accepted 16.29 g normal weight to confirm the correctness of that value. The main purpose of this paper is to direct attention to the fact that had the values for the normal weight actually found by the French investigators been adopted the French Scale and the International Scale would now be in agreement.

It is of interest to recall that the French Sugar Scale was originally based upon the rotation of 1 mm of quartz to fix the 100° point. This constant was determined by Broch to be 21° 40′ (21.667°) for sodium light. Subsequently by general usage this value was contracted to 21.67°. In converting this value (21° 40′) into degrees it is essential, from the standpoint of accuracy and clearness, that the value 21.667° should be used instead of the rounded value 21.67°, since 0.002° corresponds to 0.01°, French Sugar Scale. The 100° point, French Sugar Scale, on circular-scale instruments needs to be defined with a precision of ±0.002°. Instruments were constructed on the above basis, and when it was later found that the rotation for 1 mm of quartz was somewhat higher, namely, 21.728°, the previous value, 21.67°, was retained in order to avoid confusion of scales. This procedure necessitated the abandonment of the original definition of the 100° point for the French Scale.

The normal weight may therefore be defined as that weight of sucrose which, when made up and polarized under standard conditions, gives the same reading on a quartz compensating instrument as a quartz plate having an absolute rotation of 21.67° for $\lambda = 5892.5$ A.

The normal weight, the specific rotation $[\alpha]_D^{20}$, and the observed rotation α_D^{20} are connected by the equation

$$[\alpha]_D^{20} = \frac{100\alpha_D^{20}}{C_n \times l} \text{ or } C_n = \frac{100\alpha_D^{20}}{[\alpha]_D^{20} \times l},$$

where C_n is the concentration, or normal weight per 100 ml of solution, and l = length, in decimeters. It is, therefore, obvious that if the observed rotation is a constant (21.67°) the exact normal weight, C_n, will depend upon what value is accepted as the correct specific rotation. After a number of changes in the normal weight the value 16.29 g, weighed in air with brass weights, was officially adopted in 1896 and, as above stated, has remained the official value.

As the years have passed manufacturers of saccharimeters have improved the quality of their product until, although still based upon the same fundamental principles, the precision attainable with the modern saccharimeter has been materially increased. The best present-day saccharimeters, under optimum and carefully controlled conditions, permit a precision approaching one or two hundreths of a sugar degree.

Since it is axiomatic that a standard should be specified with an accuracy at least as great as can be attained with the instruments in connection with which it is to be used, it would seem that the value of the normal weight, 16.29 g, although probably amply good at the time it was adopted, is now in need of modification.

Since

16.29 g corresponds to 100° (French Sugar Scale),
± 0.01 g corresponds to ± 0.06° (French Sugar Scale), and
± 0.002 g corresponds to ± 0.012° (French Sugar Scale).

Therefore, in order to have the precision of the normal weight commensurate with that of the best modern saccharimeters, it should be specified with an accuracy of about ± 0.002 g. Obviously this means giving three figures after the decimal instead of rounding off to two figures. In considering this correction it should be noted that the value 16.29 g was *calculated* by Sidersky in 1885,[1] and that all subsequent experimenters have obtained values slightly lower than 16.29 g. In that year Sidersky called attention to an error in the then official normal weight of 16.19 g, and was criticized for questioning the correctness of the official normal weight.[2] Nevertheless, Sidersky had the courage of his convictions and 11 years later, in 1896, his value was made the official value. This value (16.29 g) was based upon two considerations: (1) a calculation of the normal weight using Tollens' value [3] 66.5° for the specific rotation of sucrose, whereby he obtained the value 16.295 g, and (2) the direct comparison of a Schmidt & Haensch and a Laurent saccharimeter by means of a quartz plate, which he read in both instruments. He assumed that the Schmidt & Haensch instrument was correct, since it was supposed to be directly calibrated by means of pure sucrose, and calculated the weight which would have to be used with the Laurent instrument to give the correct percentage of sugar. He found for this value 16.30 g, which confirmed his calculated value 16.295 g. It was not known at that time, as it is now that the Schmidt & Haensch instruments of those days were in error by about 0.2 percent, the 100° point then corresponding to an absolute rotation of 34.68° instead of 34.620°, as at present. Had this error been known at that time, Sidersky's experiment would have yielded a result of 0.2 percent lower, or 16.27 g. Also, as mentioned above, all subsequent determinations of the normal weight have yielded results slightly lower than 16.29 g.

Following the action of the 11^{me} Congrès International de Chimie Appliquée (Paris, 1896) in adopting 16.29 g as the official normal weight for the French Scale, a commission was appointed for the revision of the saccharimetric normal weight. This commission decided that further experimental work was required in order to establish the normal weight on a firm foundation. This work was undertaken by Mascart and Benard at the Collège de France and also by H. Pellet at the Sorbonne.

As the result of these experiments the correctness of the value 16.29 g was considered to be amply confirmed. However, Mascart and Benard [4] gave 66.54 as the specific rotation of sucrose, and 16.284 g weighed in vacuo as the normal weight. Through an error in converting this weight in vacuo to weight in air with brass weights they

[1] Bul. assn. chim. sucr. dist. **3–4**, 253 (1885–86).
[2] Bul. assn. chim. sucr. dist. **50**, 355 (1933).
[3] See footnote 1.
[4] Ann. chim. phys. **17**, 125 (1899).

arrived at the value 16.29 g, confirming Sidersky's calculation. If this error is eliminated Mascart and Benard's value becomes 16.27 g.

Also Pellet [5] gave $[\alpha]_D^{20}=66.536°$, and 16.285 g in vacuo for the normal weight. The latter corresponds to 16.27 weighed in air with brass weights.

In 1933, 38 years after his original calculation, Sidersky [6] accepts the specific rotation of 66.54° given by Schönrock [7] as the best average value and again calculates the normal weight and finds the value to be 16.282 g. This he says differs by only a negligible amount from 16.29 g. Sidersky appears to have overlooked the fact that the specific rotation calculated from Schönrock's formula which he accepts is that based upon weights in vacuo, and hence that the normal weight which he obtains is the normal weight in vacuo. Corrected to weighings in air with brass weights his figure becomes 16.272 g. If 21.667° be used, instead of 21.67° which Sidersky used, this figure is still further reduced to 16.270 g. The difference between this value and 16.29 g is not negligible, corresponding as it does to about 0.1°, French Sugar Scale.

At the eighth session of the International Commission for Uniform Methods of Sugar Analysis, 1932, the Commission in fixing the constants for the International Sugar Scale adopted the following: [8]

Normal quartz plate=100° S=34.620±0.002° (λ=5892.5 A) at 20° C. Thus the working standard used to fix the 100° S point is a quartz plate of such thickness that its rotation for sodium light is 34.620°. This standard corresponds to the procedure in the French Sugar Scale wherein the 100° point is determined by the quartz plate whose thickness is such that it has a rotation of 21° 40′ (21.667°) for sodium light. For practical purposes the 100° point in both cases is fixed by an absolute rotation. It is thus clear that in establishing both scales actual physical measurements must be made of the weights and of the rotations. It therefore makes no difference in the final results whether the weight be considered fundamental and the rotation consequential or whether the rotation be considered fundamental and the weight consequential. Both procedures if correctly carried out lead to the same result, namely, a relation between weight and rotation. In this connection, however, it should be pointed out that for the fundamental purpose of fixing the 100° S point the physical procedure indicated by the International Scale is to be preferred, among other reasons, because it gives a more open scale and accurate polarizations are easier to obtain.

A direct comparision of the two scales is therefore possible through their respective normal weights and will show how closely they are in agreement; i. e., whether the two scales actually indicate the same sugar content in a given sample.

If the effect of change in specific rotation with change in concentration is for the moment neglected the two normal weights should be in proportion to the rotations corresponding to the respective 100° points if the scales are equivalent. Hence, given the two 100° points and one of the normal weights the other may be calculated by direct proportion. Thus

$$\frac{34.620°}{21.667°}=\frac{26.000\text{ g}}{C_n}\text{ in air}=\frac{26.0159\text{ g}}{C_n}\text{ in vacuo.}$$

[5] Ann. chim. phys. **23**, 289 (1901).
[6] See footnote 2.
[7] Geiger's Handbuch der Physik **19**, 705–776 (1928).
[8] Report of the Proceedings of the Eighth Session of the International Commission for Uniform Methods of Sugar Analysis, Subject 1 (d), Int. Sugar J. **35**, 17, 62 (1933).

Solving, the normal weight, C_n, becomes 16.272 g in air or 16.282 g in vacuo. This is the value of the French normal weight required to make the two scales equivalent when the change in specific rotation with concentration is neglected.

From Schönrock's formula the change in specific rotation from 26 g to 16 g amounts to 12 parts in 66,540, corresponding to a decrease in the 16 g normal weight of about 3 parts in 16,000, thus making the required French normal weight 16.269 g in air and 16.279 g in vacuo for equivalence between the scales.

It is evident from the above that the French normal weight of 16.269 g necessary to bring the French Scale and the scale of the International Commission for Uniform Methods of Sugar Analysis into equivalence exactly equals that calculated by Sidersky, namely, 16.270 g, after due attention is paid to the obviously necessary correction for buoyancy of the air and the 100° F. S. point rotation taken as 21.667°, instead of 21.67°.

Since the 100° point of the French Scale is fixed by definition as a rotation of 21° 40′=21.667°, it is advisable to use this value to replace the less accurate value of 21.67° now used. When this change also is made the required normal weight is 16.269 g. Therefore, paralleling the definition of the International Sugar Scale, the following statement would hold for the French Sugar Scale:

(1) Normal quartz plate=100° F. S.=21.667±0.002° (λ=5892.5 A) at 20° C.

(2) The graduation of the saccharimeter shall be made at 20° C. 16.269± 0.002 g of sucrose dissolved in water, and the volume made up to 100 ml, all weighings to be made in air with brass weights, the completion of the volume and the polarization to be made at 20° C on an instrument graduated at 20° C, gives a reading of 100° F. S.

From a consideration of the foregoing it is apparent that many of the difficulties and uncertainties which have been attributed to the French Scale never had an actual existence. They have arisen through an error in adopting a normal weight which the experimental evidence did not fully justify. It should be a simple procedure to eliminate them. It is, therefore, suggested that the value 16.269 ± 0.002 g weighed in air with brass weights, be adopted as the official normal weight for the French Saccharimeter Scale. When this is done the present official normal weight of 16.29 g will have been discarded. Should this be done not only will the International Sugar Scale and the French Sugar Scale be brought into exact agreement but there will result a long-overdue recognition of the accuracy of the experimental work of those French investigators whose work was interpreted as providing a value of 16.29 g for the normal weight. It is a fortuitous circumstance that brings the two scales into complete correspondence, and it is worthy of note that these investigators, with the limited facilities available at the early date at which the work was carried out, obtained values for the specific rotation and the normal weight of sucrose identical with those obtained by the use of modern instruments and methods. The adoption of the normal weight 16.269 g as the official normal weight for the French Saccharimeter Scale would be an important development of great benefit to the sugar industry of the world.

Washington, July 3, 1936.

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STRUCTURAL CHARACTERISTICS OF SOME CONSTITUENTS OF PORTLAND CEMENT CLINKER

By Herbert Insley

ABSTRACT

Preliminary observations on the constituents of portland cement clinker by the petrographic and metallographic microscopes are recorded. The lack of purity of $3CaO.SiO_2$ in some commercial clinker is demonstrated. The structures of $2CaO.SiO_2$ in commercial clinker and laboratory preparations are illustrated, and it is suggested that differences in optical properties of specimens of dicalcium silicate may be due to twinning and not to the existence of the alpha modification at room temperatures. It has been shown that glass may be present in at least one type of cement clinker.

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I. INTRODUCTION

Recently some investigators[1] have questioned the generally accepted hypotheses that portland cement clinker is almost completely crystallized and that the compounds present are those which would crystallize when the clinker is cooled under approximately equilibrium conditions. This has led not only to a reexamination of clinker constituents by the customary methods but also to a search for improved methods.

The identification of crystalline compounds in cement clinker has been based primarily on a comparison of their optical properties with those of compounds found in phase studies of systems containing the principal oxides of which cement clinker is composed. The first phase study on this subject was that of Rankin and Wright[2] on the system

[1] F. M. Lea and T. W. Parker, Dept. Sci. Ind. Research, Bldg. Research Tech. Pap. 16 (1935). L. A. Dahl, Rock Products, p. 26 (Dec. 10, 1932).
[2] Am. J. Sci. 39, 1-79 (1915).

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CaO-Al_2O_3-SiO_2. This and later studies[3] dealing with ternary systems were the basis of Lea and Parker's investigation[4] of the quaternary system CaO–Al_2O_3–Fe_2O_3–SiO_2. The latter system includes all the essential components of portland cement clinker. Comparative studies on the actual constituents of portland cement clinker[5] show that three crystalline compounds are found which are closely similar to or identical with three of the compounds found in laboratory studies. These are $3CaO.SiO_2$, $2CaO.SiO_2$, and $4CaO.Al_2O_3.Fe_2O_3$. The relations of magnesia, an almost universal impurity in clinker, to lime, alumina and silica have been studied by McMurdie and Insley.[6]

The present investigation was, in part, an outgrowth of microscopic studies on clinker used in the manufacture of the so-called "low-heat"[7] portland cement for construction of Boulder Dam. Refinements in technique and applications of microscopic methods hitherto little used for observations on cement indicated that some constituents differed somewhat in composition from the formulas generally assigned to them. This led to a reexamination of both commercial and laboratory clinker in order that information might be obtained on the structure of the constituents, the departures from equilibrium in the cooled clinker, and the deviations from constant composition in the individual compounds. The purpose of this paper is to record the results of these examinations and to describe an extremely useful method of microscopic examination using polished specimens and reflected light.

II. METALLOGRAPHIC METHOD

1. PROCEDURE

The method of preparation and examination of specimens commonly used by the metallographer, that is, polishing a prepared plane surface on the specimen, etching with a suitable reagent, and examining with reflected light, was applied to portland cement clinker many years ago,[8] but, largely because of poor technique, the method was generally abandoned until its recent revival by Tavasci.[9]

The method of preparation and examination used is essentially as follows. Unless the clinker specimen is very dense it is generally impregnated, before grinding, with a resin[10] which is unattacked by alcohol. A flat face is then ground on the clinker specimen with coarse silicon carbide and the final grinding is done with fine emery. After careful washing the specimen is polished with a mixture of optical rouge and water on a rotating lap covered with coarse duck. The polishing is continued until the specimen is dry in order to remove any surface film of hydrated material. The specimen is then etched with a suitable reagent. After considerable experimentation a 1-percent solution of nitric acid in ethyl alcohol was found to be the best general etchant for clinker. With this reagent an etching time of somewhat less than 5 seconds is satisfactory. The speci-

[3] W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50**, 396 (1928). W. C. Hansen and R. H. Bogue, J. Am. Chem. Soc. **48**, 1261–1266 (1926).
[4] Royal Soc. Phil. Trans. [A] **234**, 1–41 (1934).
[5] P. H. Bates and A. A. Klein, Tech. Pap. BS **8** (1917) T78. L. T. Brownmiller and R. H. Bogue, Am. J. Sci. **20**, 241 (1930).
[6] J. Research NBS **16**, 467 (1936) RP884.
[7] These clinkers are characterized by fairly low CaO, high SiO_2 and a low Al_2O_3/Fe_2O_3 ratio (about 1.0).
[8] Stein, Mitt. Materialprüfungsamt, Gross-Lichterfelde, **1908**, 7. Wetzel, Verein Deut. Portland Cement Fabrik, **1913**, 5-72.
[9] Giorn. Chim. Ind. Applicata **16**, 538–552 (1934).
[10] Hyrax and Aroclor no. 4465 have been found suitable.

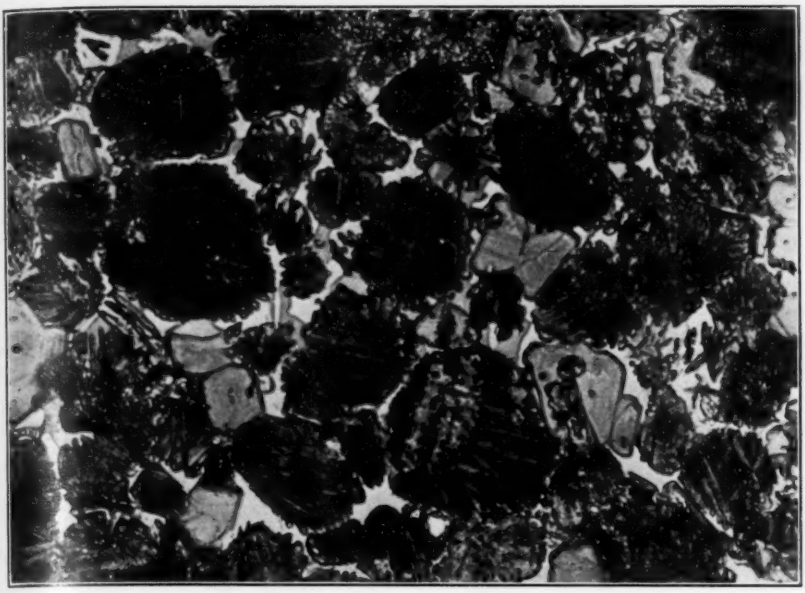

FIGURE 1.—*Low-heat clinker, brand* B.
Reflected light. Magnification 500 times.

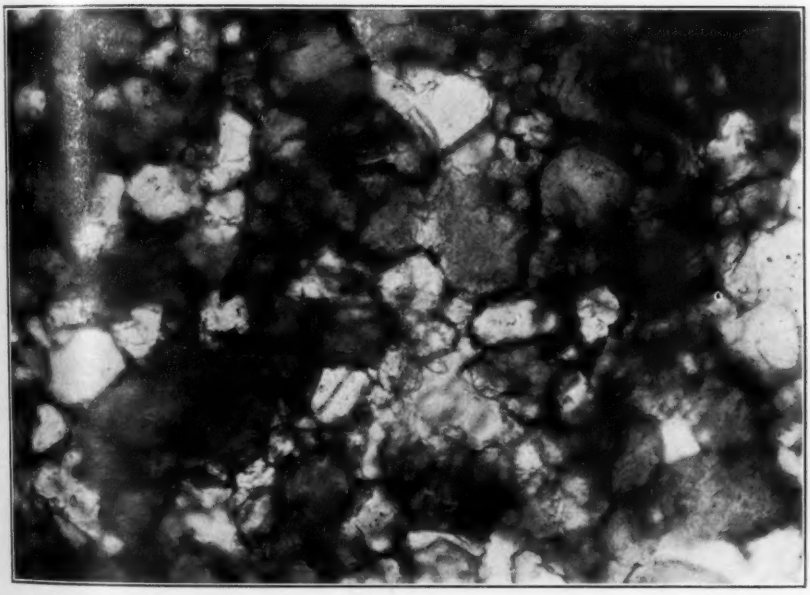

FIGURE 2.—*Low-heat clinker, brand* B.
Ordinary transmitted light. Magnification 500 times.

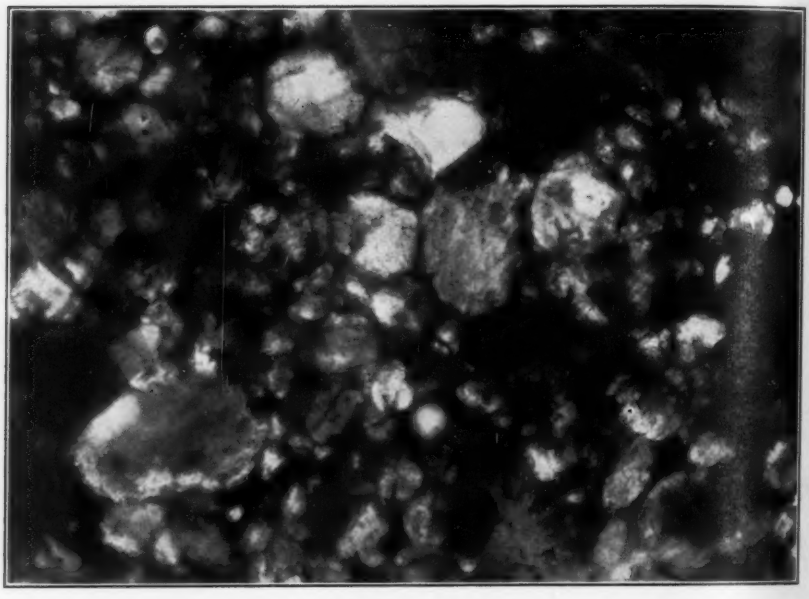

FIGURE 3.—*Low-heat clinker, brand* B.

Same field as figure 2, but with crossed nicols. Magnification 500 times.

mens are examined with a vertical illuminator using a plane glass reflector, yellow-green filter and an attached light source. For photomicrography an arc lamp is substituted for the attached incandescent lamp.

2. ADVANTAGES AND DISADVANTAGES

The method of examination of polished sections with reflected light offers several advantages over the method of thin sections with transmitted light. Thin sections are generally 20 to 30 microns thick and, since the average diameter of some of the constituents is considerably less than this range, observation suffers greatly from "overlap" of the constituents within the section. Moreover, the two interstitial constituents are so fine-grained and so closely mixed that they can be distinguished only with the greatest difficulty in thin section. Even in powder preparations viewed in transmitted light it is frequently difficult to distinguish these constituents with certainty. With polished sections, however, the object lies in a single plane and consequently boundaries of individual grains are distinct, and spatial relationships are clear. Therefore, polished sections can be used with much greater precision for quantitative areal measurements.

The contrast in clarity and definition of microscopic images of cement clinker by reflected light and by transmitted light is well illustrated by figures 1, 2, and 3. These are photomicrographs of the same brand of clinker at the same magnification. Figure 1 shows a polished, etched specimen in reflected light, figure 2 a thin section in transmitted ordinary light, and figure 3 shows the same field as figure 2 with crossed nicols.

The metallographic method has the grave disadvantage that many important optical properties of crystals in the clinker specimens cannot be measured. Primary identifications must be made either by comparison with powder preparations or thin sections on which measurements of indices of refraction, optical character, double refraction, etc., have been made, or by synthesizing the pure compounds and comparing their polished and etched surfaces with those of the cement clinker.

III. PROPERTIES OF CONSTITUENTS OF CEMENT CLINKER

By the metallographic method of examination four distinct constituents can be seen in practically all portland cement clinker (fig. 4). For this discussion they are designated A, B, C, and D.

Constituent A occurs usually as relatively large crystals with hexagonal outlines, often exhibiting zonal structure and infrequently showing simple twinning. It is strongly affected by the etching reagent.

Constituent B is present as relatively large, rounded crystals. The crystals are usually striated, sometimes with a single parallel group but more frequently with two intersecting groups of striations. This constituent, like constituent A, is strongly affected by the etching reagent.

Constituent C is a highly reflecting substance which occurs in the ground mass surrounding grains of constituents A and B. Its crystal form is sometimes difficult to distinguish, because of its habit of ag-

gregation. The crystals are generally small, often acicular. This constituent is relatively unaffected by the etching reagent.

Constituent D occurs in the ground mass surrounding crystals of A and B and intimately associated with constituent C. It has low reflecting power and is less strongly etched than constituents A and B.

1. CONSTITUENT A

This constituent occurs abundantly and usually in well-defined crystals with hexagonal outlines in normal portland cement clinker and can be readily distinguished in metallographic specimens (fig. 4). It is easily identified with the hexagonal crystals seen in thin sections and powder preparations. It has weak double refraction, a mean index of refraction of about 1.715, and negative uniaxial (or nearly uniaxial) optical character. First suspected to be tricalcium silicate by Le Chatelier,[11] it was later identified as that compound by Rankin and Wright.[12]

Petrographic, metallographic, and X-ray examinations of some commercial clinkers indicate solid miscibility in $3CaO.SiO_2$, but equilibrium studies on systems in which $3CaO.SiO_2$ occurs as a crystalline phase have not furnished substantiating evidence. Figure 5 is a photomicrograph in reflected light of a commercial clinker in which the tricalcium silicate crystals show zones or bands approximately parallel to the external faces of the crystals. Similar zonal structure, clearly seen also in figure 4, was observed by Tavasci [13] in some specimens etched with dilute hydrofluoric or nitric acid. He attributed the phenomenon to etching at too high a temperature or to failure to agitate the specimen in the etching reagent. It is not apparent how such zonal structures could be obtained in homogeneous crystals no matter how the etching reagent is used.

In thin sections of commercial clinker interference figures of tricalcium silicate frequently depart considerably from perfect uniaxiality, while sections of crystals oblique to the optic axis often exhibit a change in extinction angle from interior to exterior of the crystal.[14] Variations in indices of refraction in specimens of tricalcium silicate obtained from basic open-hearth slags have been reported by Andersen and Lee [15] and have been ascribed by them to solid solution. Crystals of $3CaO.SiO_2$ in portland cement clinker are generally so difficult to free from adhering substances that indices of refraction cannot be determined accurately.

A general shift in position of lines in the X-ray diffraction pattern of a crystalline compound in the presence of impurities as compared with a pattern of the pure compound may indicate solid solution. A small but significant shift in position may be seen in figure 6 where the pattern of a commercial clinker containing a large amount of $3CaO.SiO_2$ is compared with that of $3CaO.SiO_2$ made from pure CaO and SiO_2. Similar shifts have been observed also on other patterns of commercial clinker as well as one or two laboratory preparations. The nature of the compound taken into solution by the tricalcium silicate has not been determined.

[11] Compt. rend. **94**, 13 (1882).
[12] Am. J. Sci. **39**, 1–79 (1915).
[13] Giorn. Chim. Ind. Applic. **16**, 539 (1934).
[14] The change in extinction angle was pointed out to the author by Dr. L. S. Brown.
[15] J. Wash. Acad. Sci. **23**, 338–351 (1933). These authors attribute departures from uniaxiality to the presence of regularly oriented lamellar inclusions in $3CaO.SiO_2$. However, such inclusions are not commonly observed in portland cement clinker.

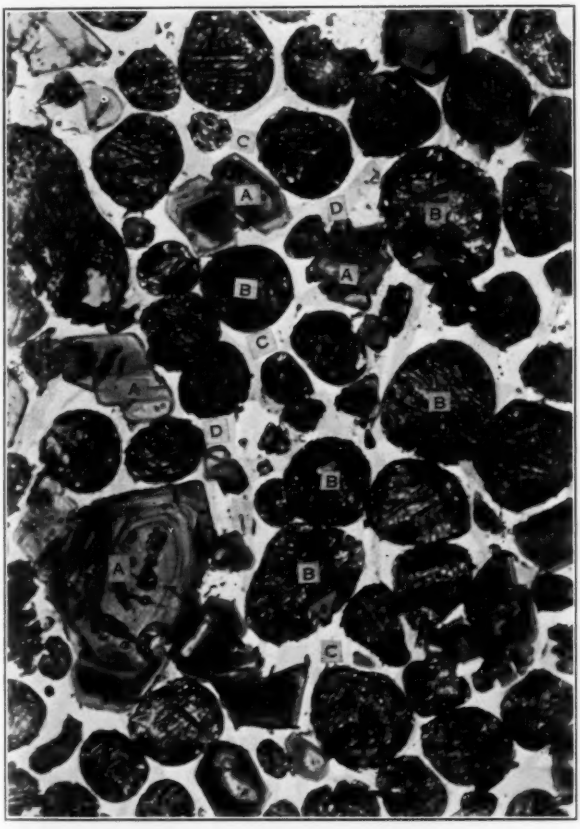

FIGURE 4.—*Low-heat clinker, brand* A.

Reflected light. Magnification 500 times. The letter designations on the photomicrograph refer to constituent designations in the text, p. 855.

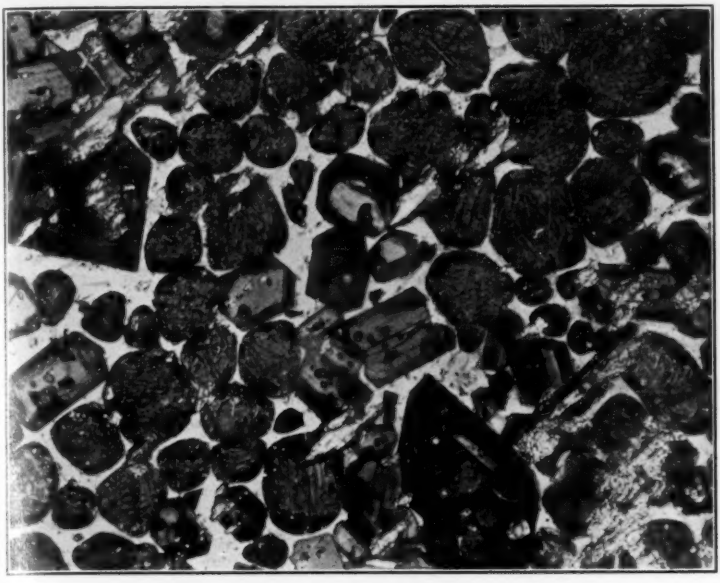

FIGURE 5.—*Low-heat clinker, brand* C.

Showing zonal structure in $3CaO.SiO_2$. A large $3CaO.SiO_2$ crystal having a single twinning plane is seen. Reflected light. Magnification 500 times.

FIGURE 6.—*Powder diffraction pattern of a cement clinker containing a large amount of* $3CaO.SiO_2$ *compared with that of pure* $3CaO.SiO_2$.

A.—Pure $3CaO.SiO_2$.
B.—Portland-cement clinker.

FIGURE 7.—*Dicalcium silicate quenched after heating at 1,450° C.*
Reflected light. Magnification 500 times.

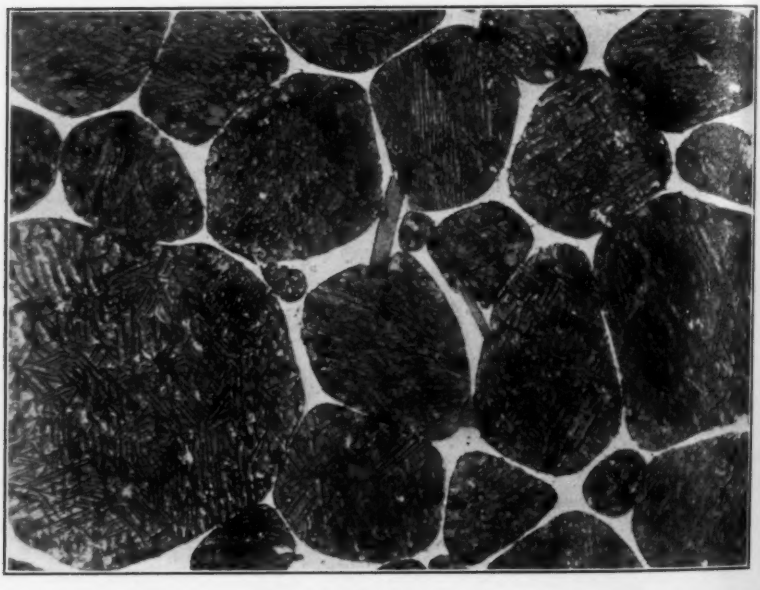

FIGURE 8.—*Twinning structure in dicalcium silicate crystals in low-heat clinker, brand* A.
Reflected light. Magnification 1,000 times.

2. CONSTITUENT B

(a) OPTICAL PROPERTIES

The compound $2CaO.SiO_2$ has long been known to be one of the principal constituents of portland cement clinker. Three forms have been identified.[16] Two of them, α and β, are presumed to be present in sound clinker. The third form, $\gamma 2CaO.SiO_2$, is found in significant quantities only in "dusted" clinker and its characteristics will not be discussed here.

Sundius[17] has measured the optical properties of α and $\beta 2CaO.SiO_2$ as they exist in portland cement clinker. He notes that the α form is characterized by two sets of fine polysynthetic twinning bands meeting at a steep angle and that the optic axial angle varies from 30 to 50° in different crystals. The β form differs from the α form slightly in indices of refraction, the optic axial angle is larger (70° or more) and twinning in samples of the β form heated below 1,420° C (the $\alpha \rightleftharpoons \beta$ inversion temperature) is characteristically a single set of polysynthetic bands. The indices of refraction of the two forms as given by Rankin and Wright and by Sundius are as follows:

	Rankin and Wright	Sundius
$\alpha 2CaO.SiO_2$	$\alpha_{Na} = 1.715 \pm 0.002$ $\gamma_{Na} = 1.737 \pm 0.002$	$\alpha = 1.719 \pm 0.001$ $\gamma = 1.733 \pm 0.001$
$\beta 2CaO.SiO_2$	$\alpha_{Na} = 1.717 \pm 0.002$ $\gamma_{Na} = 1.735 \pm 0.002$	$\alpha = 1.717 \pm 0.001$ $\gamma = 1.736 \pm 0.001$

It is significant that the differences in values between the two forms as given by each observer are practically within the limits of precision specified.

It is worthy of note that the complicated twinning found in the so-called "α" form is almost universally present and that, therefore, optical properties very probably are measured on twinned grains. Twinning bands are generally exceedingly narrow, often less than a micron in width (figs. 7 and 8). Since corresponding principal vibration directions are inclined symmetrically in adjacent twinning bands, it is evident that indices of refraction in principal vibration directions measured by the immersion method on such grains may be considerably in error. The apparent optic axial angle and the apparent double refraction also may vary considerably, because of differences in the number and width of twinning bands. The possibility seems to have been overlooked that crystals of $2CaO.SiO_2$ as found in clinker as well as in laboratory preparations may all be in the β state, and that the complex twinning often cited as indicative of the α state may be in reality only an indication that the crystal has at some time been in the α state. The production of twinning as a result of passing from one polymorphic state to another on cooling is well known.[18]

To substantiate this, samples of $2CaO.SiO_2$ were made and mixed with the stabilizing substances used by Sundius (Cr_2O_3, $3CaO.Al_2O_3$, and $3CaO.SiO_2$). Specimens were mixed also with a small amount (0.2 percent) of B_2O_3. These were heated in either a platinum-resistance furnace or an oxyhydrogen blowtorch to temperatures well

[16] G. A. Rankin and F. E. Wright, Am. J. Sci. 39, 1–79 (1915).
[17] Z. anorg. allgem. Chem. 213, 343–352 (1933).
[18] H. Le Chatelier, The Constitution of Hydraulic Mortars, p. 53 (McGraw-Hill Book Co., New York, 1906).

above 1,450° C and quenched in ice water or mercury. A comparison of their X-ray powder patterns with samples of the same material heated at 1,375° C showed complete identity in number, position, and intensity of lines.

(b) TYPES

Twinning in $2CaO.SiO_2$ is exhibited in transmitted polarized light as parallel bands with extinction inclined in opposite directions in adjacent bands. In reflected light the twinning appears as parallel striations. A sample of $2CaO.SiO_2$ containing 0.2 percent of B_2O_3 after heating at 1,450° C and quenching in mercury is shown in figure 7. Individual grains show at least two and sometimes three sets of interpenetrating striations, each set being composed of parallel bands. A mixture of CaO, Al_2O_3, Fe_2O_3, and SiO_2 in the proportions characteristic of some "low-heat" clinker, and which had been heated to 1,450° C and quenched, showed the same complicated striations in the dicalcium silicate (fig. 9). A polished section of commercial low-heat clinker as received from the manufacturer is shown in figure 8. This type of twinning has generally been considered characteristic of $\alpha 2CaO.SiO_2$. It will here be called type I.

Dicalcium silicate heated below 1,420° C frequently occurs as grains having a single set of polysynthetic bands. A sample containing 0.2 percent of B_2O_3 heated at 1,375° C and quenched in mercury shows parallel striations in reflected light (fig. 10). Figure 11 shows this type of banding as found in a sample of laboratory clinker of the same composition as that shown in figure 9 but heated at 1,375° C instead of 1,450° C. We may call this $2CaO.SiO_2$ of type II. Commercial clinkers made in rotary kilns rarely contain dicalcium silicate of type II.

Still a third type, which we may designate as type III, is found in commercial as well as synthetic clinker. It appears to be untwinned, but it is frequently found as overgrowths on grains of type I. In commercial clinker type III frequently occurs as irregular grains with what appear to be veinlets or cracks running through them. This is shown clearly in figure 12, in which $2CaO.SiO_2$ of type III occurs both as individual grains and as small rounded inclusions in $3CaO.SiO_2$. Figure 13 shows still another clinker in which layers of type III are overgrown on type I. Another photomicrograph of this clinker (fig. 1) shows fingers of $2CaO.SiO_2$ extending into the matrix material, apparently a result of crystallization during cooling. In experiment with laboratory preparations the untwinned form was obtained only when moderately slow cooling below the $\alpha \rightleftharpoons \beta$ inversion temperature was permitted before quenching. Figure 14 is a photomicrograph of a sample of laboratory clinker allowed to cool from 1,375 to 1,275° C before quenching. Small individual elongated grains of type III and overgrowths of type III on type II are visible. Petrographic examination of these specimens shows the presence of untwinned crystals with moderate double refraction and with indices of refraction approximately those of α or $\beta 2CaO.SiO_2$.

In general, these observations confirm those of Tavasci [19] on the structural characteristics, although no evidence has been obtained in the present work to support his rather broad generalizations concerning the occurrence of solid solution of other substances in $2CaO.SiO_2$.

[19] Giorn. Chim. Ind. Applic. **16**, 538–552 (1934).

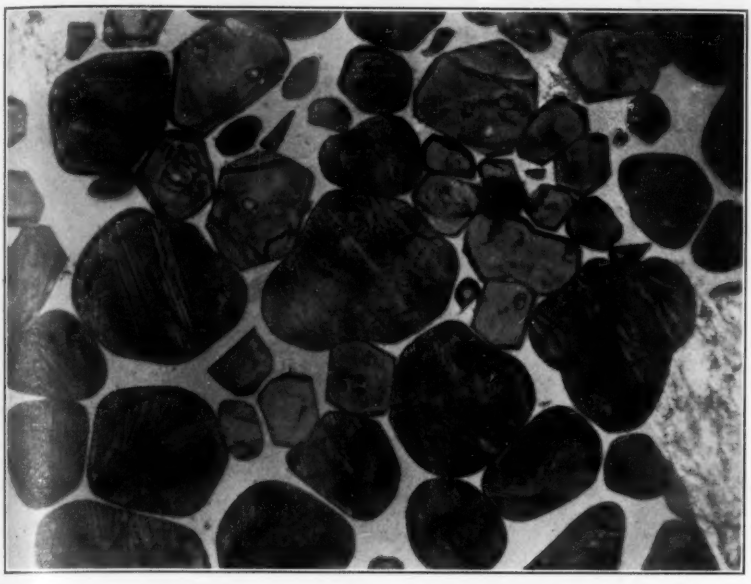

FIGURE 9.—*Laboratory-prepared low-heat clinker, quenched after heating to 1,450° C.*
Reflected light. Magnification 500 times.

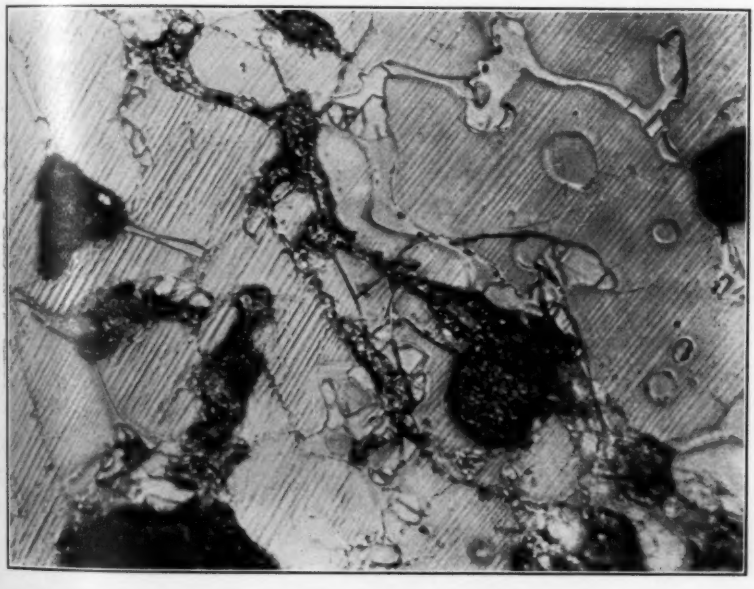

FIGURE 10.—*Dicalcium silicate containing 0.2 percent of* B_2O_3 *quenched after heating to 1,375° C.*
Reflected light. Magnification 1,000 times.

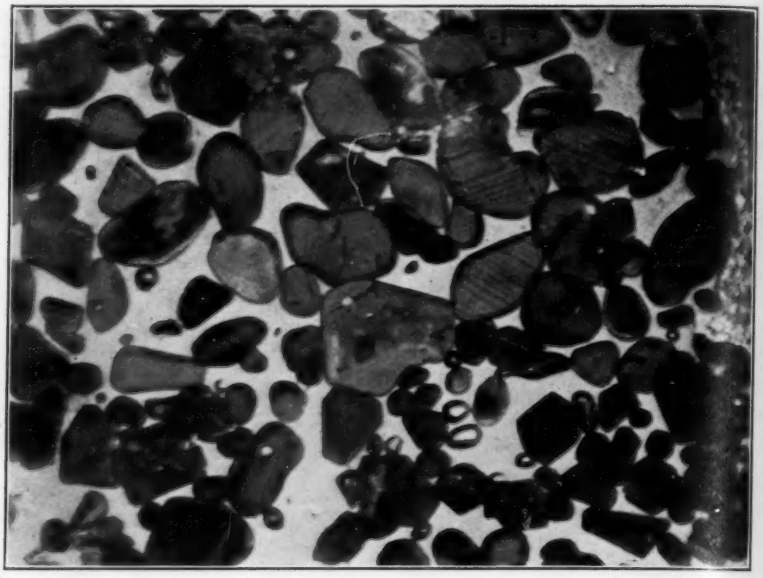

FIGURE 11.—*Laboratory-prepared low-heat clinker quenched after heating at 1,375° C.*
Reflected light. Magnification 500 times.

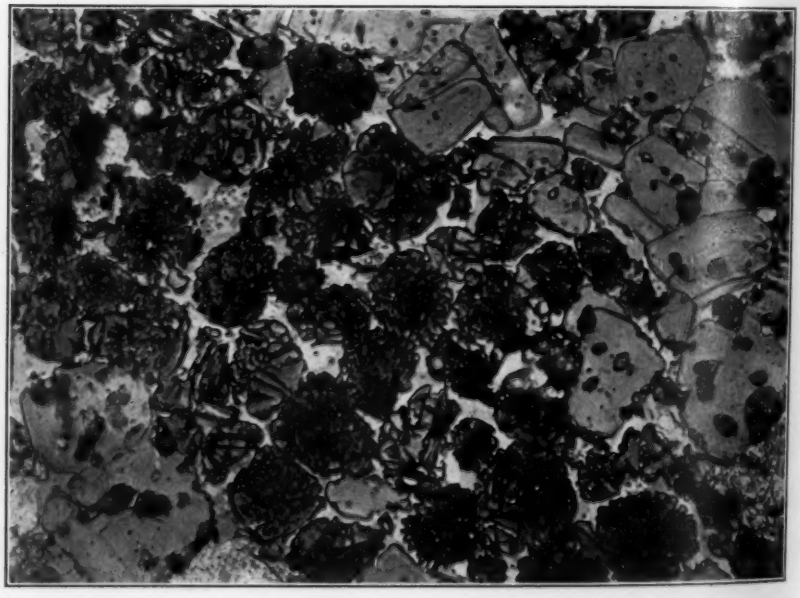

FIGURE 12.—*Dicalcium silicate of type III in low-heat clinker of brand D.*
Reflected light. Magnification 500 times.

FIGURE 13.—*Overgrowths of type III dicalcium silicate on type I in low-heat clinker of brand* B.

Reflected light. Magnification 1,000 times.

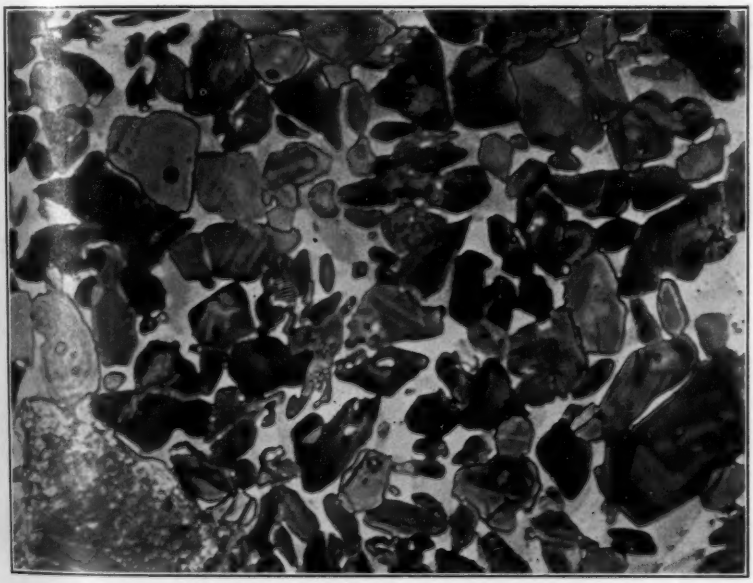

FIGURE 14.—*Laboratory prepared low-heat clinker quenched after cooling slowly from 1,375 to 1,275° C.*

Showing $2CaO.SiO_2$ of types II and III. Reflected light. Magnification 500 times.

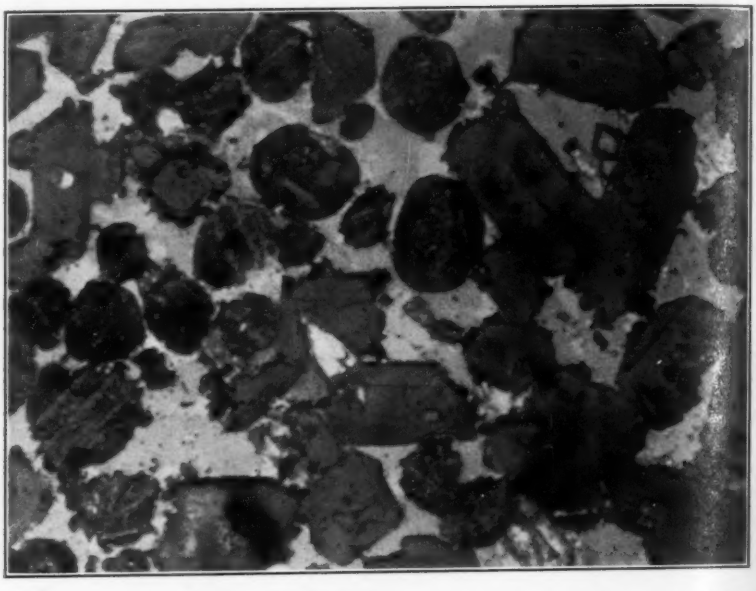

FIGURE 15.—*Normal portland cement clinker with* Al_2O_3/Fe_2O_3 *ratio of 2.5.*
Reflected light. Magnification 500 times.

3. CONSTITUENT C

The third constituent of portland cement clinker has been identified as $4CaO.Al_2O_3.Fe_2O_3$ by optical properties and diffraction patterns.[20] It is seen in reflected light as highly reflecting grains associated with the fourth constituent in the matrix surrounding grains of $3CaO.SiO_2$ and $2CaO.SiO_2$ (fig. 2 and 4). This constituent sometimes occurs as crystals with distinctly prismatic habit but more frequently as aggregates of irregular shape. It is evidently identical with the compound which is observed with transmitted light in thin sections or powder preparations as interstitial grains having high indices of refraction (mean index about 2.03), moderately strong double refraction, weak to strong pleochroism, and frequently prismatic habit. Aggregates of crystals of this compound in cement clinker may be resolved by examination with crossed nicols in reflected light, using an intense illuminant such as an arc lamp, where the difference in extinction position in the individual crystals is exhibited.

$4CaO.Al_2O_3.Fe_2O_3$ is known to become decidedly more pleochroic in the presence of MgO and presumably the MgO must enter into solid solution. Schwiete and zur Strassen [21] limit the solid solution of MgO in $4CaO.Al_2O_3.Fe_2O_3$ to 2 percent in the binary system. Their method is based on the relative intensity of lines in the X-ray patterns and appears to be susceptible of large errors. Some preliminary experiments in this laboratory indicate that the maximum solid solubility of MgO in $4CaO.Al_2O_3.Fe_2O_3$ is less than 1 percent. The extent of solution of other clinker compounds in $4CaO.Al_2O_3.Fe_2O_3$ is practically unknown. Indirect evidence is that it is small.

4. CONSTITUENT D

The composition of the fourth constituent of portland cement clinker has not been determined with certainty. Tricalcium aluminate is present in mixtures of CaO, Al_2O_3, Fe_2O_3, and SiO_2 which lie within the range of portland cement compositions and which have been completely crystallized under equilibrium conditions. In commercial clinker, however, the identification by microscopic methods is doubtful. By X-ray patterns this compound has been identified only in clinkers which contain Al_2O_3 in greater than normal amounts.[22]

In polished etched specimens observed by reflected light constituent D is found to occur in the matrix of clinker intimately associated with $4CaO.Al_2O_3.Fe_2O_3$ (figs. 1, 2, 4, and 15). It etches less readily than tricalcium silicate or dicalcium silicate and has much lower reflectivity than $4CaO.Al_2O_3.Fe_2O_3$. In examining the low-heat clinkers used for cements for Boulder Dam it was found that the constituents were well differentiated, even the interstitial constituents being readily distinguished with the metallographic microscope.

In most specimens of commercial clinker the interstitial material cannot be resolved microscopically in thin sections, and even in powder preparations it is often difficult to distinguish between $4CaO.Al_2O_3.Fe_2O_3$ and the intimately associated constituent D. In powder preparations of the Boulder Dam cement it was found that the constituent closely associated with $4CaO.Al_2O_3.Fe_2O_3$ was isotropic, with an index

[20] W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, J. Am. Chem. Soc. **50**, 396 (1928). L. T. Brownmiller and R. H. Bogue, BS J. Research **5**, 813 (1930) RP233.
[21] Zement **23**, 511-514 (1934).
[22] L. T. Brownmiller and R. H. Bogue, Am. J. Sci. **20**, 241 (1930).

of refraction of about 1.64. The index was too low for $3CaO.Al_2O_3$ and did not correspond well to any probable crystalline compound. Therefore, the constituent was presumed to be glass. Since $3CaO.Al_2O_3$ is frequently the last compound to crystallize, the difference in composition between it and the glass resulting from more rapid cooling is not great. The ratio of constituent D to constituent C is related roughly to the ratio Al_2O_3/Fe_2O_3. This is indicated by a comparison of figures 14 and 15, the clinker represented in figure 14 having an Al_2O_3/Fe_2O_3 ratio of 1.0 and that in figure 15 having a ratio of 2.5.

Further investigations are in progress in an attempt to identify constituent D in other types of clinker, particularly by developing etching reagents which will give positive distinctions between $3CaO.Al_2O_3$ and the glass which may be present.

5. ACCESSORY CONSTITUENTS

Free CaO is frequently present in small amounts in cement clinker either as a result of incomplete combination during clinkering or because of improper batch composition. It occurs typically in rounded isotropic grains and usually as inclusions in A (tricalcium silicate) and in B (dicalcium silicate). Because of its high refractive index (1.83) it is readily distinguished in thin sections. In specimens prepared for metallographic observation free CaO is etched by dilute nitric acid more readily than other constituents and appears as minute rounded pits.

Since free MgO occurs as isotropic grains with an index of refraction (1.736) very near that of the other principal clinker constituents it is not as readily identified as is free CaO. In polished and etched specimens free MgO appears as small grains, sometimes rounded and sometimes with visible octahedral outlines, but always lacking perceptible internal structure. It is noteworthy that in many cement clinker specimens which contain as much as 4 percent of MgO no crystals of magnesia can be observed even with the most painstaking examination. It is not known whether this amount of MgO is taken into solid solution by other crystalline compounds or whether it is dissolved in glass present in the clinker. This problem is now being studied.

IV. QUANTITATIVE MEASUREMENTS

Quantitative measurements of the relative amounts of the various constituents present in cement clinker are of considerable value in understanding the composition of the constituents, because systematic deviations from calculated compound composition may indicate solid solution or incomplete crystallization. The metallographic method, utilizing one of the integrating micrometer stages,[23] is particularly suitable for quantitative measurements because of elimination of overlap of crystals and the possibility of accurate setting on the crystal boundaries. Preliminary measurements on two types of clinker indicate that the $3CaO.SiO_2$ content is higher by microscopic analysis than by calculation from chemical composition and that the amount of constituent D is less than the calculated amount of $3CaO.Al_2O_3$. This problem is being studied further by quantitative measurements on clinker specimens which have been analyzed chemically.

[23] C. K. Wentworth, J. Geol. 31, 228–232 (1923).

V. SUMMARY

The metallographic method of microscopic examination using polished and etched specimens, when combined with the usual petrographic methods, aids considerably in determining the composition of the crystalline constituents of portland cement clinker.

The four major constituents of cement clinker are differentiated easily by the metallographic method. The characteristic structures and modes of occurrence of each major constituent are described and illustrated.

The tricalcium silicate crystals in many cement clinkers are not pure $3CaO.SiO_2$, but give evidence by three methods of examination that they contain significant quantities of other material in solid solution.

The twinning structures in dicalcium silicate depend in part on the temperature to which they have been heated and the method of cooling. The apparent divergence in optical properties of specimens of $2CaO.SiO_2$ heated under different conditions may be due to the presence of twinning bands and not to the actual existence of the α form at room temperature.

In some types of commercial portland cement clinker glass is present and tricalcium aluminate is absent. Evidence as to the existence of $3CaO.Al_2O_3$ in normal commercial portland cement clinker is questionable.

Quantitative microscopic measurements of the relative amounts of constituents may be of considerable value in the determination of the nature of the constituents.

WASHINGTON, June 22, 1936.

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ELECTROLYTIC MEASUREMENT OF THE CORROSIVENESS OF SOILS

By I. A. Denison

ABSTRACT

The electrolytic behavior of steel in contact with 47 soils of known corrosiveness was studied by means of a cell in which both electrodes were steel and the electrolyte was moist soil. By providing differential aeration of the electrodes the cell was enabled to develop its own electromotive force. Measurements were made of the voltage, current, and resistance of such cells. The relation between the current density and applied voltage was also studied. The losses in weight of the test specimens were related to the average current density over a certain range of applied voltage and to the total quantity of electricity produced in the corrosion process. The corrosion of the specimens in the laboratory tests was correlated with corrosion experienced in long-time field tests. The results of the tests may be applied practically in predicting the corrosiveness of soils toward iron and steel. However, they cannot be applied to the prediction of leaks or to the estimation of the useful life of a section of pipe line until the relations connected depth of pitting with exposed area and time can be established.

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I. INTRODUCTION

Corrosion of metals in soils is accompanied by a flow of current, which discharges into the soil at the anodic or corroding areas and returns to the metal surface at the cathodic areas. Since corrosion proceeds as a result of the action of electrolytic cells, the design of a suitable corrosion cell might be considered the first step in the study of soil corrosion in the laboratory by electrical methods. The cell should preferably be so designed that corrosion could proceed naturally; that is, by the cell developing its own electromotive force (emf). From measurements of voltage and current in such a cell it should be possible to determine what external voltage might be applied without

materially altering the nature of the corrosion process occurring within the cell. The significance of the results obtained from such a study, particularly from the standpoint of corrosion testing, would depend largely upon the maintenance of those conditions of moisture and aeration that prevail in the natural soil, so far as these conditions can be reproduced in the laboratory and incorporated in a general corrosion test.

The primary purpose of this study was to determine whether the relative corrosiveness of soils toward steel could be predicted from measurements of the electrical properties of corrosion cells in which various soils constituted the electrolytes. A successful electrolytic test should render unnecessary the determination of separate factors in corrosion, such as hydrogen-ion concentration, total acidity, and concentration of soluble salts. The influence on the rate of corrosion of such factors should be manifested in the electrical properties of the corrosion cells. From measurements of current and potential of appropriate cells, either with an impressed emf or with only the internal emf associated with differences in aeration it should be possible to arrange soils in about the same order of their corrosiveness as is found from loss-of-weight tests conducted for short periods in the laboratory, and from long-time field tests.

II. PROPERTIES OF SOILS

The samples of soil used in this study were taken from the 47 original test sites selected by the National Bureau of Standards in its investigation of soil corrosion and described in its first report.[1] The soil samples were prepared by drying and crushing the aggregates in a mortar and passing them through a no. 20 sieve. Care was taken to avoid reducing the size of the soil aggregates below that necessary to pass the sieve, in order to preserve, as far as possible, their natural structure.

Water extracts of the soils were prepared as follows: A suspension of soil and water in the ratio of 1:5 was shaken mechanically at intervals for a total of 24 hours during a period of 72 hours. The extract was decanted into a 250-ml, tall-form beaker and was filtered through a Berkfeld filter (12 by 2.5 cm) into a pressure flask by suction. The extracts were analyzed by the methods described by Collins.[2]

Hydrogen-ion concentration was measured colorimetrically after 18 hours in a separate extract, using a 1:2 soil-water ratio. Portions of each indicator were adjusted isohydrically to the acid, midpoint, and alkaline ranges to avoid altering the pH value of the extract. Total acidity was determined by methods previously described by the writer.[3] The resistivity of each soil was determined by means of a wheatstone bridge, using 60-cycle, alternating current. The soil samples were saturated with water, mixed thoroughly, and allowed to stand several hours before being tested. The values of resistivity were corrected to 60° F (15.6° 3). The moisture equivalent was determined in the usual manner,[4] that is, by saturating a 30-g sample with water, subjecting it to a centrifugal force of 1,000 times gravity

[1] K. H. Logan, S. P. Ewing, C. D. Yeomans. Tech. Pap. BS **21**, (1928) T368.
[2] W. D. Collins. Water Supply Paper 596-H, U. S. Geological Survey (1928).
[3] I. A. Denison. BS J. Research **10**, 413 (1933) RP539.
[4] L. J. Briggs and J. W. McLane. Am. Soc. Agron. **2**, 138 (1910).

for 40 minutes, and determining the residual water content by drying in an oven at 105° C. The moisture equivalent is a measure of the retentiveness of a soil for water and is an index of the texture of the soil. It has been shown to represent the condition in nature of a soil which after saturation has come into equilibrium with gravitational and capillary forces.[5,6] A significant feature of the moisture equivalent with respect to corrosion is that it represents the condition at which the finer pore spaces within a soil are filled with water, the larger spaces with air.

The determined properties of the soils are shown in table 1. The soils are grouped in two classes according to their reactions. Within each class the arrangement is in the order of increasing resistivity. The classification according to reaction is somewhat arbitrary since there are no criteria for the exact separation of soils on the basis of acidity or alkalinity. For instance, although soil 28 has a slightly acid reaction, it is an "alkali" if not an "alkaline" soil, in the terminology of soil investigators. Analyses of the water-soluble materials in most of the acid soils were not made because of the very low concentrations of soluble material in these soils.

Table 1 illustrates the remarkably wide range in the properties of the soils studied. In texture, the soils range from the coarsest sands to the heaviest clays; in pH, from the high acidity of pH 3.1 to marked alkalinity (pH 9.5); and in soluble material, from concentrations as high as several percent to very low concentrations. Special classes of soils such as peat, muck, and "tidal marsh" are also represented.

[5] C. S. Schofield and C. W. Wright. J. Agr. Research **37**, (1928).
[6] W. W. Burr and J. C. Russell. Bien. Rep. Nebr. Dept. Pub. Works, p. 199 923-24).

TABLE 1.—*Properties of soils*

[mg-eq=milligram equivalent]

ALKALINE SOILS

Soil	Soil type	Location	Moisture equivalent	pH	Total acidity per 100 g of soil	Resistivity at 60° F	Composition of water extract per 100 g of soil						
							Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
			%		mg-eq	ohm-cm	mg-eq	m -eq	mg-eq	mg-eq	mg-eq	mg-eq	mg-eq
45	Unidentified alkali	Casper, Wyo	14.8	7.4	(a)	263	8.15	3.70	0.70	0.00	0.24	0.18	11.98
23	Merced silt loam	Buttonwillow, Calif	24.7	9.4	(a)	278	8.38	.38	.22	.02	1.87	1.12	5.57
13	Hanford very fine sandy loam	Bakersfield, Calif	21.7	9.5	(a)	290	6.23	.09	.13	.00	1.12	1.64	3.76
8	Fargo clay loam	Fargo, N. Dak	37.0	7.6	(a)	350	1.42	1.72	2.55	.00	.71	.01	4.43
28	Montezuma clay adobe	San Diego, Calif	24.6	6.8	(b)	408	1.50	.06	.18	.00	.12	.99	.89
15	Houston black clay	San Antonio, Tex	51.4	7.5	5.0	489	2.18	.88	.20	.00	2.00	.13	.73
27	Miller clay	Bunkie, La	42.6	6.6	3.7	570	.53	1.86	1.12	.00	2.00	.08	1.54
2	Bell clay	Dallas, Tex	37.6	7.3	3.5	684	.28	1.09	.13	.00	1.18	.04	.18
30	Muscatine silt loam	Davenport, Iowa	29.4	7.0	2.6	1,300	.32	.65	.40	.00	.71	.09	.24
5	Dublin clay adobe	Oakland, Calif	28.8	7.0	6.5	1,346	.93	.48	.10	.00	.60	.03	.25
18	Knox silt loam	Omaha, Nebr	28.4	7.3	1.4	1,410	.27	.63	.20	.00	.94	.00	.25
46	Unidentified sandy loam	Denver, Colo	7.6	7.0	(b)	1,500	(b)	(b)	(b)	(b)	(b)	(b)	(b)
47	Unidentified silt loam	Salt Lake City, Utah	25.7	7.6	3.0	1,770	.67	.72	.39	.00	.88	.06	.48
25	Miami clay loam	Milwaukee, Wis	25.8	7.2	4.7	1,780	.23	.70	.41	.00	1.01	.03	.10
35	Ramona loam	Los Angeles, Calif	18.0	7.3	5.7	2,060	.68	.68	.49	.00	1.10	.06	.35
20	Mahoning silt loam	Cleveland, Ohio	22.4	7.5	1.5	2,870	.25	.48	.20	.00	.51	.00	.15
26	Miami silt loam	Springfield, Ohio	16.4	7.3	2.6	2,980	.27	.50	.31	.00	.70	.03	.12
12	Hanford fine sandy loam	Los Angeles, Calif	12.4	7.1	2.5	3,190	.39	.50	.16	.00	.40	.00	.14
32	Ontario silt loam	Rochester, N. Y	17.8	7.3	.5	5,700	.23	.70	.12	.00	.73	.01	.42

ACID SOILS

43	Tidal marsh	Elizabeth, N. J.	55.4	3.1	36.8	60	45.10	5.17	9.45	0.00	0.00	43.30	37.00
33	Peat	Milwaukee, Wis.	72.8	6.8	36.0	800	1.52	7.30	4.06	.00	(b)	2.27	2.13
40	Sharkey clay	New Orleans, La.	33.0	6.0	9.4	970	.56	.58	.44	.00	.93	.07	.28
44	Wabash silt loam	Omaha, Nebr.	31.2	5.8	8.8	1,000	1.05	1.08	.66	.00	1.97	.82	.41
1	Allis silt loam	Cleveland, Ohio	28.6	7.0	11.4	1,215	.72	.25	.43	.09	.09	.09	.83
29	Muck	New Orleans, La.	34.5	4.2	28.1	1,270	2.15	1.92	1.55	.00	.00	1.69	2.30
41	Summit silt loam	Kansas City, Mo.	33.1	5.5	11.0	1,320	.30	.54	.36	.00	.78	.04	.46
19	Lindley silt loam	Des Moines, Iowa	28.4	4.6	10.9	1,970	.38	.32	.41	.00	16	.03	.46
7	Unidentified silt loam [a]	Cincinnati, Ohio	34.3	4.4	29.8	2,120							
21	Marshall silt loam	Kansas City, Mo.	31.2	6.2	9.5	2,370							
9	Genesee silt loam	Sidney, Ohio	24.8	6.8	7.2	2,820							
14	Hempstead silt loam	St. Paul, Minn.	17.2	6.2	5.6	3,520							
34	Penn silt loam	Norristown, Pa.	23.4	6.7	7.0	4,900							
22	Memphis silt loam	Memphis, Tenn.	28.4	4.9	9.7	5,150							
17	Keyport loam	Alexandria, Va.	30.8	4.5	19.1	5,980							
4	Chester loam	Jenkintown, Pa.	22.2	5.6	7.6	6,670							
39	Sassafras silt loam	Wilmington, Del.	24.2	5.6	6.6	7,440							
10	Gloucester sandy loam	Middleboro, Mass.	13.0	6.6	3.6	7,460							
16	Kalmia fine sandy loam	Mobile, Ala.	22.2	4.4	11.8	8,200							
11	Hagerstown loam	Baltimore, Md.	32.0	5.3	10.8	11,000							
36	Ruston sandy loam	Meridian, Miss.	13.8	4.5	4.6	11,200							
37	St. Johns fine sand	Jacksonville, Fla.	7.0	3.8	15.3	11,200							
24	Merrimac gravelly sandy loam	Norwood, Mass.	13.0	4.5	12.6	11,400							
42	Susquehanna clay	Meridian, Miss.	34.8	4.7	28.2	13,700							
31	Norfolk sand	Jacksonville, Fla.	2.8	4.7	1.8	20,500							
3	Cecil clay loam	Atlanta, Ga.	29.1	5.2	11.5	30,000							
38	Sassafras gravelly sandy loam	Camden, N. J.	3.0	4.5	1.7	38,600							
6	Everett gravelly sandy loam	Seattle, Wash.	12.2	5.9	12.8	45,100							

[a] Alkaline.
[b] Not determined.
[c] Previously classified erroneously as Fairmount silt loam.

III. DESCRIPTION OF CORROSION CELL

The corrosion cell consisted essentially of two steel electrodes separated by a layer of moist soil as electrolyte, the whole being contained within a brass ring, which formed part of the external circuit. By aerating the electrodes differentially the cell was enabled to develop its own emf. This effect was accomplished by using as cathode a steel screen which was more readily accessible to air than the anode. In order that the accessibility of air to the cathode would be determined by the natural permeability of the soil, the cathode was covered by a layer of soil of definite thickness and with a definite moisture content.

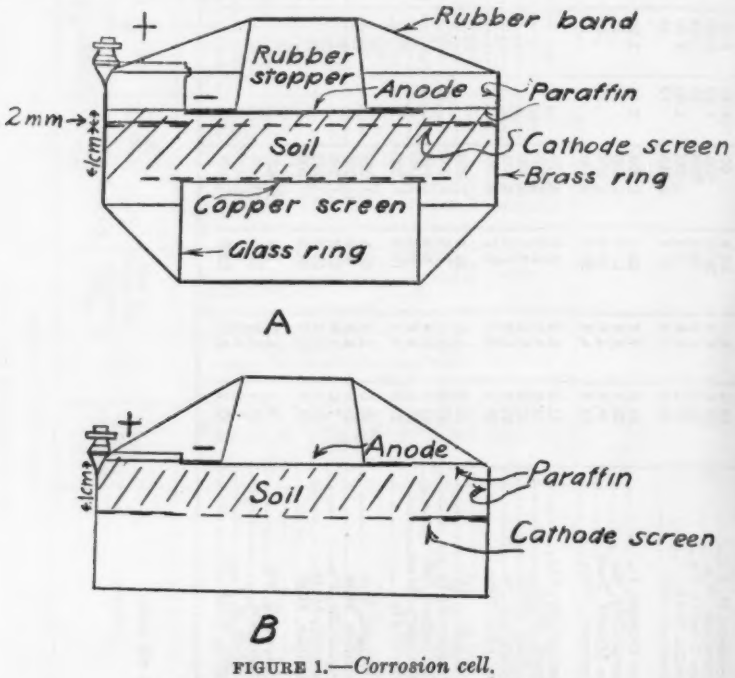

FIGURE 1.—*Corrosion cell.*

A. Cathode covered by soil; B. Cathode exposed to air.

Because of differential aeration the cathode attained a more positive potential. Consequently, when the circuit was closed, ferrous ions entered the soil at the anode, and at the cathode an equivalent quantity of hydrogen ions was discharged or otherwise consumed. The current flowed in the external circuit from the cathode through the brass ring to which it was connected by solder, completing the circuit to the anode through the binding post and the copper wire attached to the anode. Since the brass ring was insulated from the soil by a layer of paraffin, its function in the electrical circuit was merely as a conductor of current in the external circuit. The cell is shown diagrammatically in figure 1. The parts of the cell are shown in figure 2.

Both of the electrodes consisted of low-carbon steel. Since the cathode screen was not attacked, but simply served as the electrode upon which a reducing action took place, it was considered unneces-

FIGURE 2.—*Parts of corrosion cell.*

A, Glass ring; B, cell; C, rubber stopper; D, copper screen; E, rubber band; and F, specimen.

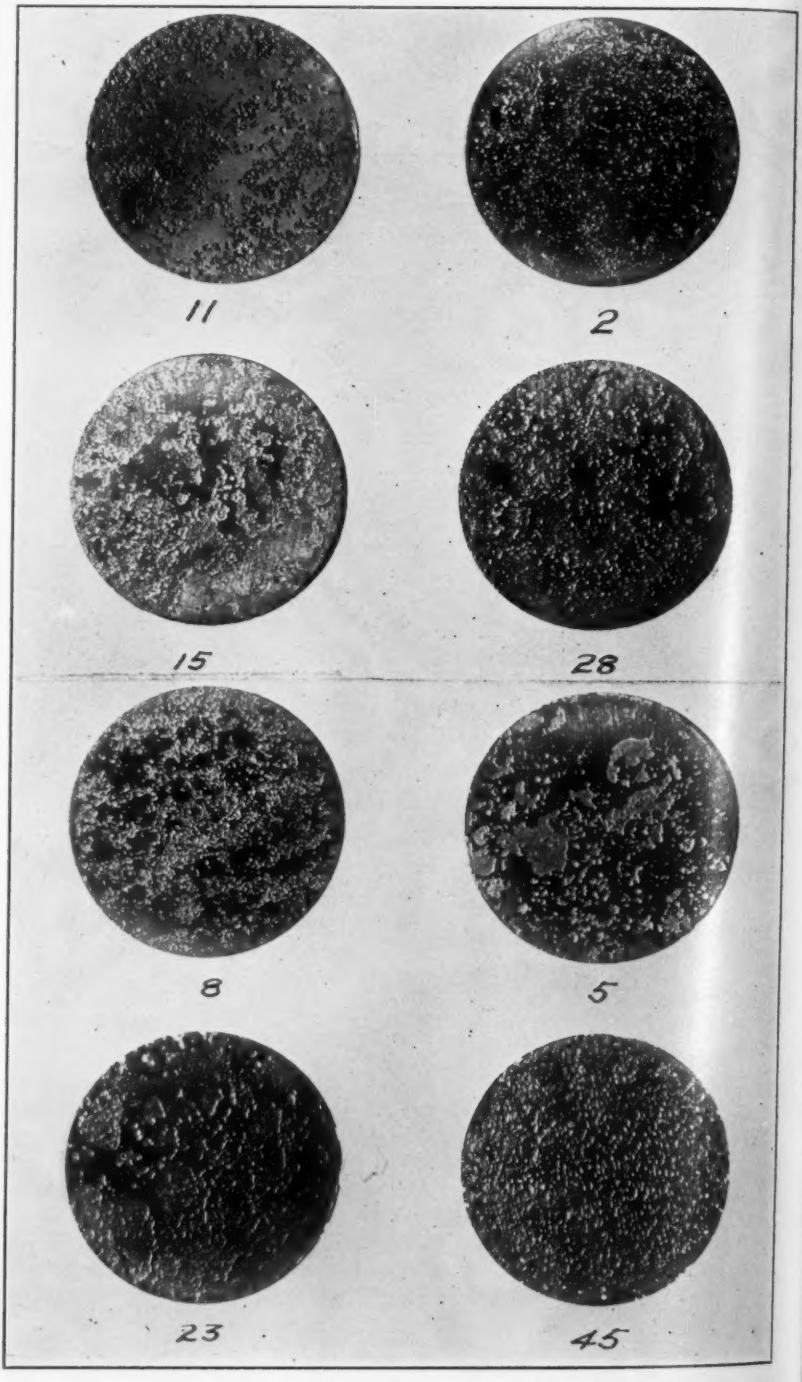

FIGURE 3.—*Appearance of corroded specimens after 14 days in laboratory corrosion test.*

Soil 11. Hagerstown loam, Baltimore, Md.
2. Bell clay, Dallas, Tex.
15. Houston black clay, San Antonio, Tex.
28. Montezuma clay adobe, San Diego, Calif.

Soil 8. Fargo clay loam, Fargo, N. Dak.
5. Dublin clay adobe, Oakland, Calif.
23. Merced silt loam, Buttonwillow, Calif.
45. Unidentified alkali soil, Casper, Wyo.

sary to make it of steel identical with that of the anode. The latter was a disk 45 mm in diameter and 0.3 mm thick. The cathode, which was a 16-mesh screen (6 mesh/linear centimeter) having wires 0.46 mm in diameter, was soldered across the brass ring or container 1 cm from the top. The brass ring was 75 mm in diameter, 25 mm high, and 1 mm thick.

Electrical connection between the anode and cathode was made through a binding post on the brass ring by means of a copper wire soldered to the back of the anode. In order to restrict, as far as possible, the current flow to straight lines normal to the surface of the cathode, the apparent area of the latter was made equal to the area of the anode. This was accomplished by insulating the border of the screen and the inner surface of the ring with a layer of paraffin. The actual area of the screen, calculated from the length and diameter of the wires, was almost exactly twice the apparent area.

Each anode specimen was cleaned by means of alcohol and ether. The original surface of one face was then removed by rubbing with 1G French emery paper in opposite directions, rotating the disk through an angle of 90° and repeating the process. The copper wire was soldered to the back of the disk, and the prepared surface of the latter was recleaned by rubbing with filter paper moistened with distilled water. The disk was weighed to the nearest milligram and the reverse surface was covered with two coats of lacquer.

The procedure used in setting up the cell was as follows: The cell was inverted and the space of 1 cm above the cathode was filled with dry soil, which was compacted by means of a brass cylinder weighing about 500 g. The soil was prevented from running through the screen by placing a layer of muslin over the upper surface of the screen and moistening it with a few drops of water. Sufficient distilled water was added to the soil to bring it to the moisture equivalent. The soil layer was held in firm contact with the cathode by inserting a circular piece of copper gauze and a glass ring between the soil and a rubber band wrapped around the cell. With the cell resting on the glass ring, the section of the cell between the anode and cathode was filled with soil to a depth of 2 mm and moistened in the manner described, and the disk placed in position. The surface of the soil surrounding the disk was covered with a thin layer of melted paraffin. The disk was maintained in firm contact with the soil by inserting a rubber stopper between the disk and the rubber band, as shown in figure 1. The circuit was closed by attaching the copper wire to the binding post. The cell was placed in a 1-quart (0.95 l) friction-top can in which a small quantity of water was poured to provide a saturated atmosphere. After closing the lid the can was placed in a chamber and maintained at 30± 0.5° C for 14 days.

At the conclusion of the test period the disks were cleaned and the lacquer was removed by means of a wire brush. When necessary to remove rust, the disks were immersed for a few minutes in a warm 10-percent solution of ammonium citrate made alkaline with ammonia. Corrosion products not removed by this treatment were removed with the point of a knife blade. The disks were reweighed and the loss in weight was expressed as average penetration. All tests were run in duplicate, and tests for which the duplicates did not agree

within 20 percent were repeated. Typical corroded specimens are shown in figure 3.

For the practical testing of soils certain modifications in the dimensions of the cell and in the procedure for setting up the cell may be suggested. The height of the cell should be so chosen that when the cell is filled with moist soil and the anode is placed in position, the electrodes be separated by a layer of soil 2 mm thick and the cathode well shielded from the atmosphere by a layer of soil 1 cm thick. The diameter of the cell should be so reduced that it would be only slightly greater than the diameter of the disk.

In order to avoid the necessity of determining in advance the proper quantity of water to apply to each soil, it would be preferable to presaturate the soil contained in the cell and to bring it approximately to the moisture equivalent by the application of suction. From a recent study [7] of soil moisture relations, based on energy considerations, it appears that the moisture equivalent can be attained by suction produced by means of a Buchner funnel and a water pump. The desired pressure is maintained by pouring a thin suspension of silt on the filter paper before the soil is applied. The silt layer allows water to pass readily through it but entirely prevents the flow of air. This method of producing the moisture equivalent could be readily adapted to the corrosion test.

IV. MEASUREMENTS WITH APPLIED EMF

1. METHOD

The method used for studying the current density-potential relation in soils was essentially that described by Blum and Rawdon.[8] According to this method the potentials applied to the cell are adjusted to produce certain desired current densities. The corresponding potential differences between the electrodes are measured after they have become steady, which was usually attained in from one to three hours. The current densities are then plotted against the cell potentials (corrected for IR drops if these are significant). The relative corrodibility of various metals in a given solution, or of the same metal in different solutions, is inferred from the relative positions and shapes of the current density-potential curves. This method with slight modifications was employed by Ewing in [9] testing the corrosiveness of a limited number of soils from the National Bureau of Standards test sites.

In the present study, current density-potential measurements were made after the cells had been on closed circuit from 24 to 36 hours. It was found that at least 24 hours' standing was necessary for the electrodes to become stabilized. The effect on the measurements of longer standing was not studied. The current density was increased by definite steps, and the voltages across the cell were corrected for IR drops. The current density at each step was maintained for 10 minutes, by which time the voltage had become steady. After each voltage reading, the resistance of the cell was quickly determined. This practice was made necessary by the marked increase in resistance with current density that was shown by many

[7] R. K. Scofield. Trans. 3d Int., Cong. Soil Sci. 2, 37 (1935).
[8] W. Blum and H. S. Rawdon. Trans. Am. Electrochem. Soc. 52, 402 (1927).
[9] S. P. Ewing. Am. Gas Assn. Mo. 14, 356 (1932).

of the cells. A steady current density was maintained despite an increasing resistance of the cell, by placing 10 000 ohms resistance in series with the cell and using 110 volts d–c, with a rheostat as a potential divider.

2. CURRENT DENSITY-POTENTIAL MEASUREMENTS

The relation between current density and the applied voltage is shown in figure 4 for typical soils. Because the cells develop their own emf, the curves do not usually pass through the origin. The

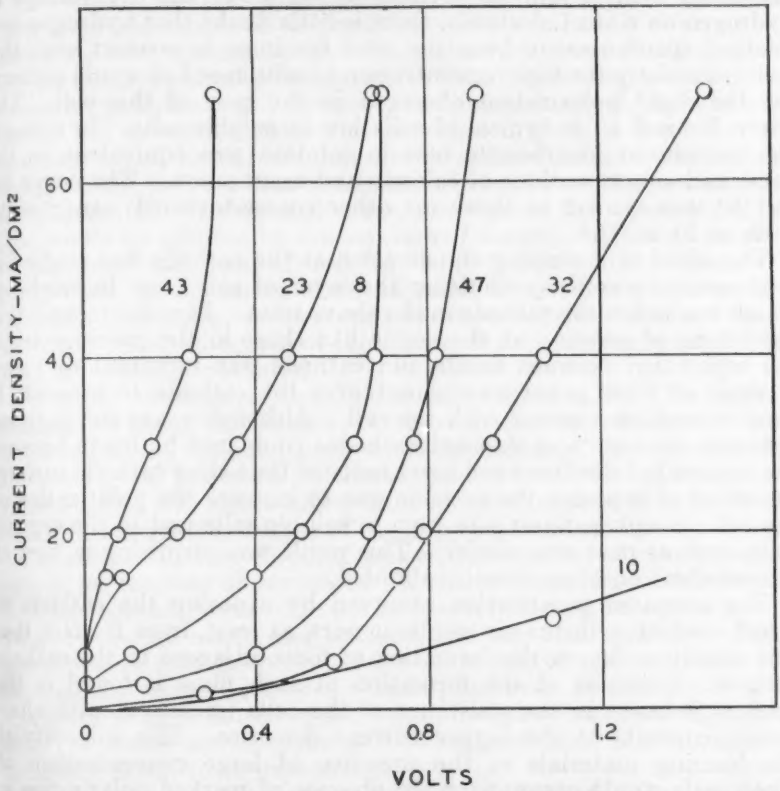

FIGURE 4.—*Current density-potential curves of typical soils when an external electromotive force is applied*

Soil numbers are designated on the curves

curves indicate the departure of the potentials of the anode and cathode from their equilibrium potentials in the soils as the current densities on the electrodes are increased, and are therefore indicative of the total polarization of the cells at various current densities.

The relative positions of the curves would be expected to indicate the relative corrosiveness of the soils. Thus a small potential difference, such as 0.2 volt, which for any reason might develop on steel surfaces, would produce in contact with soil 10 a very slight current density and a corresponding low rate of corrosion, but with soil 43 a very high current density and rate of corrosion. From another point of view the potential required to produce a current density of say

20 ma/dm² would be only 0.1 volt in soil 43, but an impossibly high value in soil 10. As will be seen later, the relative corrosiveness of soils both with respect to field and laboratory tests can be predicted by comparison of their current density-potential curves.

The positions of the curves for the soils tested can be explained in a general way on the basis of the properties of the soils, as given in table 1. Thus very little polarization would be expected in soil 43, owing to the fact that it has a pH of 3.1, a total acidity of 36.8 me-eq per 100 g of soil, and a specific resistance of but 60 ohm-cm. Since increasing acidity and salt concentration lower the overvoltage of hydrogen on a steel electrode, there is little doubt that hydrogen was evolved spontaneously from the steel specimen in contact with this soil. Similarly the high concentration of salts in soil 23 would account for the slight polarization observed in the case of this soil. The curve for soil 32 is typical of soils low in soluble salts. In this soil the content of bicarbonate ions in solution was equivalent to the combined concentrations of calcium and magnesium. The curve for soil 10 was similar to those for other coarse-textured, sandy soils, such as 31 and 38.

The effect of increasing the aeration at the cathode was studied in representative soils by omitting the layer of soil 1 cm in thickness which was below the cathode in the above tests. In order to maintain conditions of aeration at the anode like those in the previous tests, the separation between anode and cathode was increased to 1 cm. A sheet of filter paper was placed over the cathode to separate it from immediate contact with the soil. Although exact comparisons between the bare and shielded cathodes could not be made because the removal of the lower soil layer reduced the active cathode surface, the effect of exposing the cathode was to increase the polarization of the cell (except in those soils high in soluble salts and in the organic soils, such as peat and muck). This result was surprising in view of the excellent aeration thereby afforded.

The increased polarization observed by exposing the cathode to direct contact with the air results in part, at least, from the fact that this condition favors the formation of films adjacent to the cathode surface. Evidence of the formation of such films is found in the marked increase in the resistance of the cells (measured with alternating current) at the higher current densities. The solubility of film-forming materials in the presence of large concentrations of alkali salts would account for the absence of marked polarization in soils 23, 28, and 45 on exposing the cathode to the air. Marked reduction in polarization in exposing the cathode was observed in the case of muck (soil 29), peat (soil 33), and soil 37, which was a mixture of quartz sand and organic matter. The effect of covering the cathode by a layer of organic matter is to increase polarization, because the oxygen present in the pore spaces is largely consumed in oxidizing the organic matter instead of acting as a depolarizer at the cathode.

V. MEASUREMENTS WITHOUT APPLIED EMF

The voltage developed by the corrosion cells is due to differences in the concentration of oxygen at the surface of the electrodes. On the addition of water to soil contained in a test cell, ferrous ions initially enter the soil from both electrodes, and the hydrogen depos-

ited on each electrode tends to be removed by combination with oxygen. On closing the circuit, current flows from the disk to the screen through the soil, because the greater concentration of oxygen in contact with the screen produces a more positive potential, the screen thereby becoming cathodic. From a somewhat different point of view, the flow of current from disk to screen may be considered to result from the lower concentration of hydrogen on the latter, since current necessarily flows toward that surface on which the concentration of hydrogen is less.

In view of the fact that the surfaces of ordinary ferrous metals show a certain degree of air passivity and are naturally covered by a thin oxide film, the maximum voltage of a corrosion cell will probably not be developed until breakdown of the oxide film has occurred. However, as Britton and Evans[10] have pointed out, there is, in addition to the primary distribution of corroded areas, a secondary distribution which is dictated largely by differential aeration and the disposition of the corrosion products. It would seem, therefore, that the distribution of corroded areas, and hence the potential of the disk, would be affected by the aeration of the soil. With an excess of oxygen at certain parts of the disk, as is the case in a porous, well-aerated soil, precipitation of an adherent film of ferric hydroxide in immediate contact with the metal at certain points of incipient breakdown will result in repair of the film and the maintenance of a low (i. e., more noble) potential.

Since the potential of the disk at any time would be the average potential of the attacked and protected areas, the maximum voltage of the cell would depend largely upon the nature of the soil contained in the cell. As corrosion continues, the accumulation of ferrous and ferric ions at the anode along with other electrode changes would tend to diminish the voltage of the cell by polarization.

The current flowing through the corrosion cell is, of course, related directly to the rate of corrosion. If the cell should function ideally, all of the current generated in the corrosion process would pass through the soil between anode and cathode, and the total quantity of electricity flowing over the period of the test would be an exact measure of the quantity of steel corroded. Since, however, local circuits on the anode are usually active in corrosion, at least in soils of high resistivity, an exact correspondence between corrosion and quantity of electricity is not to be expected.

The relation between current and voltage in these cells depends on the resistance and polarization of the cells. The cell resistance is in turn dependent on the active area of the electrodes and the resistance of the soil, which may be modified by the deposition of corrosion products on the electrodes and in the soil mass. The active areas of the electrodes do not correspond to the actual areas because corrosion does not proceed uniformly over the surface of the anode, but from small breaks or pinholes in the slightly protective oxide film. Initially the resistance of the circuits is relatively great because the anodic areas are small, but as these areas extend and become more numerous the resistance tends to decrease, unless it is increased by deposition of corrosion products. The effect of polarization has been previously shown in connection with the study of the current-density potential relation with applied voltage.

[10] S. C. Britton and U. R. Evans. Trans. Electrochem. Soc. 61, 441 (1932).

1. METHODS

Measurement of the electrical properties of the corrosion cells with no applied emf were made at frequent intervals on the cells previously used for the current density-potential measurements. The latter measurements were made 18 hours after the cells were set up. For the first few days measurements were made daily, after which they were made on alternate days. After 2 weeks the cells were taken down and the losses in weight of the disks were determined.

The voltages of cells of low internal resistance, i. e., below 100 ohms, were measured by means of a voltmeter having a resistance of 10 000 ohms. For cells of higher resistance a voltmeter having a resistance of 1 000 000 ohms per volt was used. When the external resistance of the circuit is very high the terminal voltage of the cell is substantially the same as the emf and corrections are unnecessary. The current was measured with a milliammeter, and the resistance with a wheatstone bridge and a 60-cycle, alternating-current galvanometer. The current was read first and the voltage and resistance immediately afterward.

2. MEASUREMENTS WITH THE CATHODE COVERED BY A LAYER OF MOIST SOIL

The average voltage of each cell was between 20 and 150 mv with an average for all cells of about 100 mv. The maximum voltage during the test period, usually 150 to 200 mv, was reached within 18 hours, and the voltage then declined to as low as 10 mv at the expiration of the test. In some soils the polarity of the cell did not become established for several days, after which there was a slow increase instead of a decrease in voltage. The cells containing the organic soils 29, 33, and 37 did not acquire a definite polarity during the test period. In view of the tendency for the organic matter in these soils to absorb oxygen, it is probable that insufficient oxygen reached the gauze to produce a significant difference in potential between it and the disk. Typical current-time curves for various soils are shown in figure 5.

The marked differences in the curves in figure 5 are to be attributed primarily to differences in the solubility of the corrosion products in various soils. Because of the greater solubility of hydroxides of iron in acid soils and in soils containing chlorides and sulfates, the corrosion products readily diffuse away from the anode. This diffusion prevents the formation of protective films and allows corrosion to continue. The curve for soil 28 is typical of soils such as 23 and 45, in which the soluble material is chiefly alkali chlorides and sulfates. The curve for soil 17 is typical of strongly acid soils, such as 7 and 43. Since at the same pH the solubility of ferric hydroxide is much less than that of ferrous hydroxide, the current in a well aerated soil would be expected to be less than in a poorly aerated soil. The small current associated with soil 3, which at the moisture equivalent is well aerated, was caused by the precipitation of ferric hydroxide in the vicinity of the points of attack, and the resultant increase in the resistance of the cell. The precipitation of corrosion products directly over the points of attack in well-aerated soils such as sands, in contrast to the diffu-

sion of the products of corrosion in poorly drained soils, accounts in part for the great difference in corrosiveness shown by these two classes of soils.

A second factor which tends to diminish the flow of current in the cells is the deposition of protective films near the cathode. In alka-

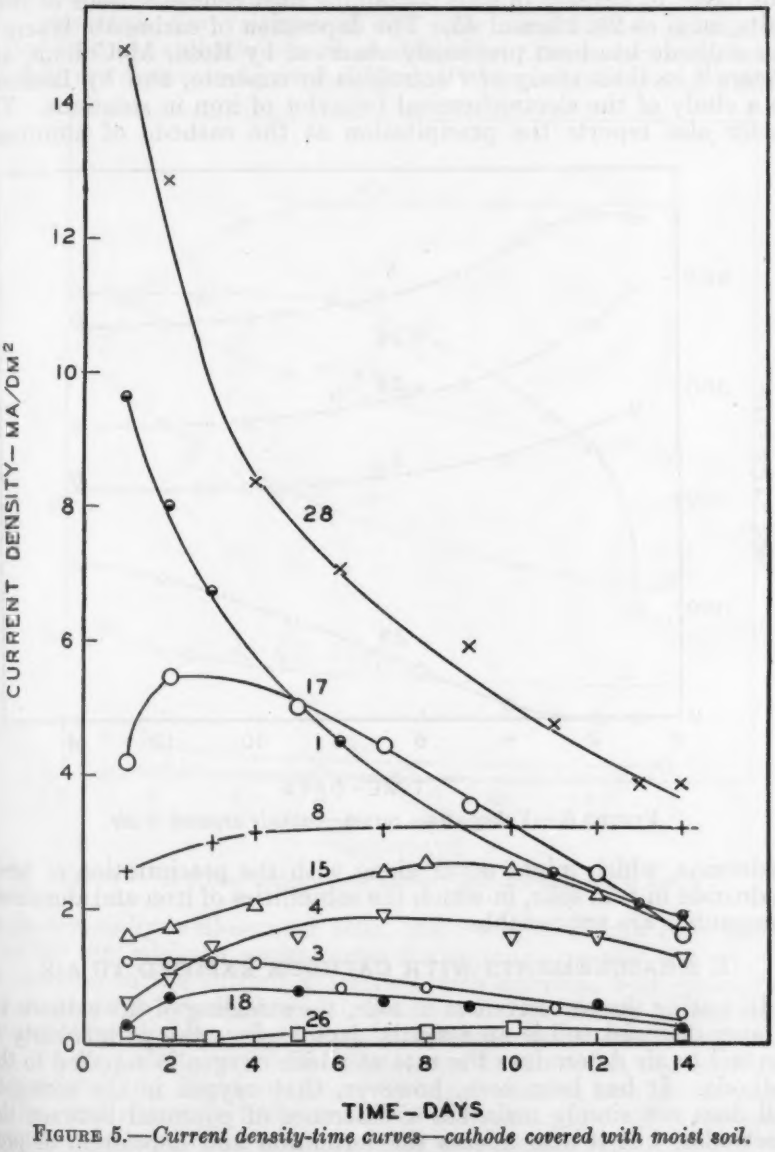

FIGURE 5.—*Current density-time curves—cathode covered with moist soil.*

line soils these films are formed by the concentration at the cathode of calcium and magnesium ions and of hydroxyl ions (produced by reduction of oxygen). Carbon dioxide, which is produced in the soil by bacterial activity, leads to the formation of films of calcium and magnesium carbonate. The carbonate films reduce the current flow

by reducing the accessibility of oxygen to the cathode, that is, by polarization; and by increasing the resistance of the corrosion circuits. Since as shown by Baylis,[11] the solubility of calcium carbonate is much greater at a given pH in solutions of sodium chloride and sodium sulfate than in pure water, protective carbonate deposits are not likely to develop in soils containing high concentrations of these salts, such as 23, 28, and 45. The deposition of carbonate layers at the cathode has been previously observed by Rosa, McCollum, and Peters [12] in their study of electrolysis in concrete, and by Lochte [13] in a study of the electrochemical behavior of iron in solutions. The latter also reports the precipitation at the cathode of aluminum

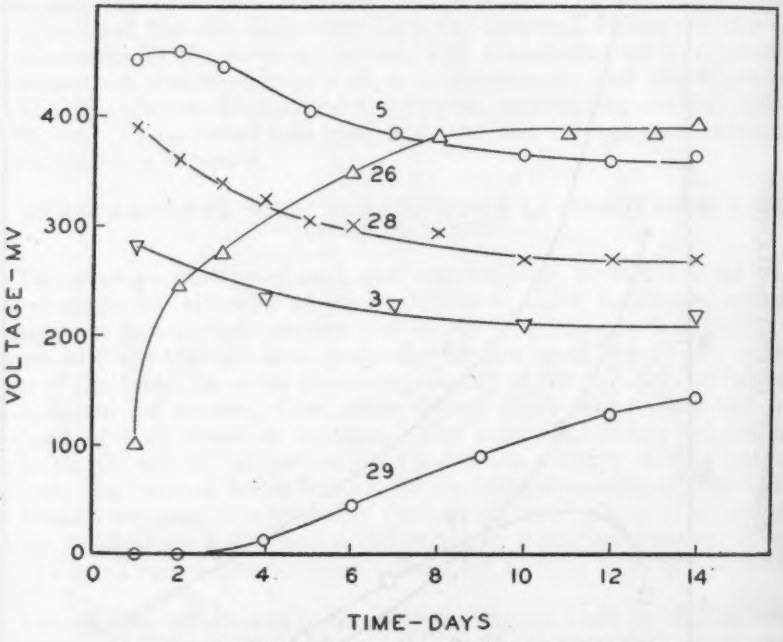

FIGURE 6.—*Voltage-time curves—cathode exposed to air.*

hydroxide, which might occur along with the precipitation of ferric hydroxide in acid soils, in which the solubilities of iron and aluminum compounds are appreciable.

3. MEASUREMENTS WITH CATHODE EXPOSED TO AIR

In testing the corrosiveness of soils, the shielding of the cathode by a layer of moist soil is an essential factor, since the permeability of the soil to air determines the rate at which oxygen is supplied to the cathode. It has been seen, however, that oxygen in the corrosion cell does not simply maintain a difference of potential between the electrodes, but it also affects the formation and deposition of protective films of corrosion products. To obtain additional information on the effect of the degree of aeration on the behavior of the

[11] J. R. Baylis. J. Am. Water Works Assn. 12, 211 (1924). F. N. Speller. Corrosion—Causes and Prevention (McGraw-Hill Book Co., New York, 1926).
[12] E. B. Rosa, Burton McCollum, and O. S. Peters. Tech. Pap. BS 2, (1913) T18.
[13] H. L. Lochte. Trans. Electrochem. Soc. 64, 173 (1933).

cell, cells were set up in which the cathodes were exposed directly to the atmosphere. From measurements on such cells, in which the tendency toward film formation at the cathode would be intensified, the effects of aeration could be more readily studied. In order not to affect the aeration of the anode, the distance between cathode and anode was increased to 1 cm.

As predicted, the voltages of the cells were almost invariably greater with the cathode bare than shielded. Curves for representative soils are shown in figure 6. Except in organic soils, such as 29,

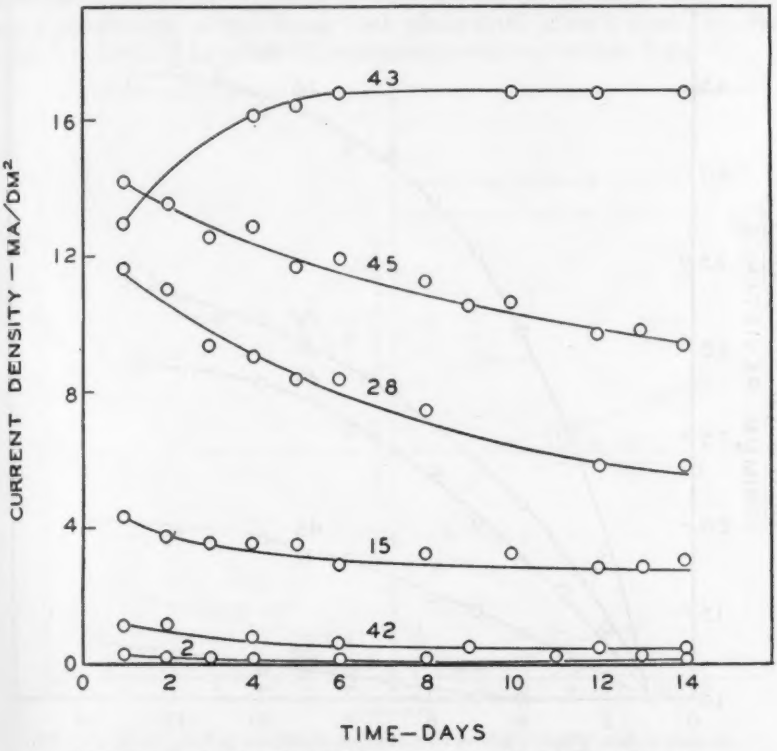

FIGURE 7.—*Current density-time curves—cathode exposed to air.*

and in especially well-aerated soils, the voltages of the cells were above 200 mv, while in several cases the voltage exceeded 450 mv.

A decrease in the current associated with corrosion can generally be accounted for by an increase in polarization, as shown by current density-potential measurements, or by an increase in cell resistance. Thus, the cells containing soils 43, 45, and 28, in which the current flow was large (fig. 7), showed very little polarization at high current densities, and relatively little change in cell resistance. The reverse was true for cells in which small currents were measured.

Figure 8 illustrates the change in resistance of cells containing representative soils. The marked change in resistance of alkaline soils, such as 20, is produced by the precipitation of carbonates of calcium and magnesium on the cathode and in the pores of the filter paper in contact with the cathode. Evidence of the formation of

carbonate films is found in the active effervescence of the soil on the cathode and filter paper on treatment with acid. The detection of such films in soils which do not naturally contain carbonates is, of course, proof of their formation at the cathode by the electrolytic action of the cell.

The chemical compositions of the extracts of the alkaline soils (table 1) are generally consistent with the values for current and resistance. Thus, in soils 28 and 45, illustrated in figures 7 and 8, the excess of alkali chlorides and sulfates would be expected to

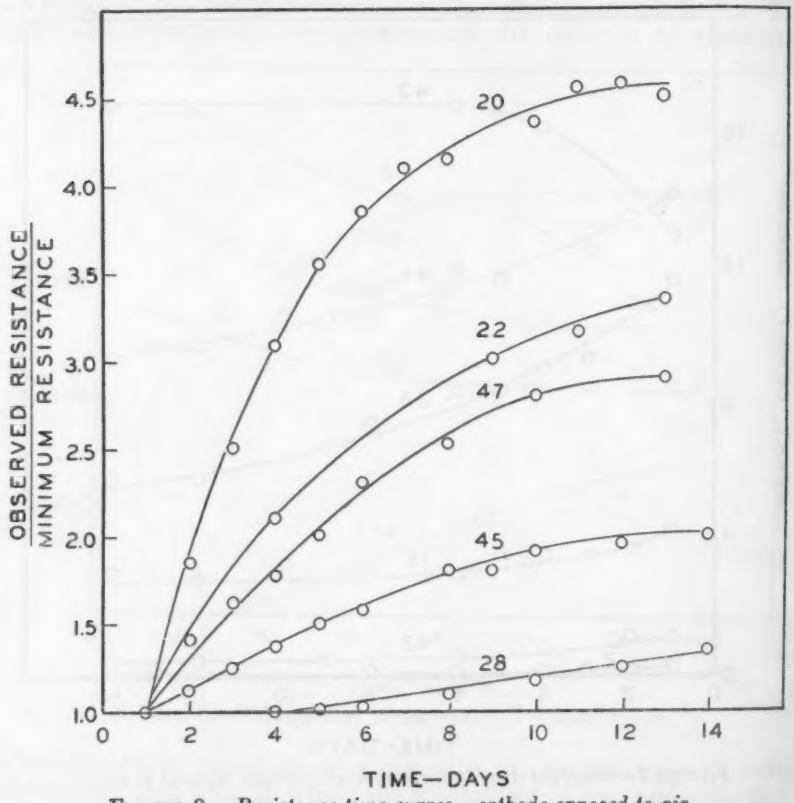

FIGURE 8.—*Resistance-time curves—cathode exposed to air.*

prevent the formation of carbonate films; whereas in soil 2 the quantity of such salts is insignificant. The excess of alkali salts over the alkaline earths in soil 15 indicates the probability of partial protection, such as is illustrated by the curve for this soil in figure 7.

The very small current associated with soil 42 (fig. 7) and the marked change in resistance shown in figure 8 for soil 22, indicate that film formation at the cathode may have occurred, even in these acid soils, for example, by concentration of ions of iron and aluminum at the cathode and their precipitation as hydroxides.

The effect of aeration of alkaline soils (2 and 23) upon the formation of protective films at the cathode was studied by setting up cells with the moisture content at saturation instead of at the moisture equivalent. The results are shown in figure 9.

The curves for soil 2 are typical of the alkaline soils with relatively low resistivity, in which the soluble material consists chiefly of calcium, magnesium and bicarbonate ions. The curves for soil 23 are typical of the alkali soils, in which the soluble material is chiefly sulfates and chlorides of the alkali metals. The difference in current for soil 23 at moisture equivalent and at saturation is not great but for soil 2 this difference is enormous, and very little current flows in the cell at the lower moisture content. The reason for such marked differences is seen when the change in resistance with time for the two soils is compared. In soil 23, with the soil at moisture equivalent, very little change in resistance took place until after 1 week, whereas in soil 2 a fivefold increase in resistance occurred within 3 days.

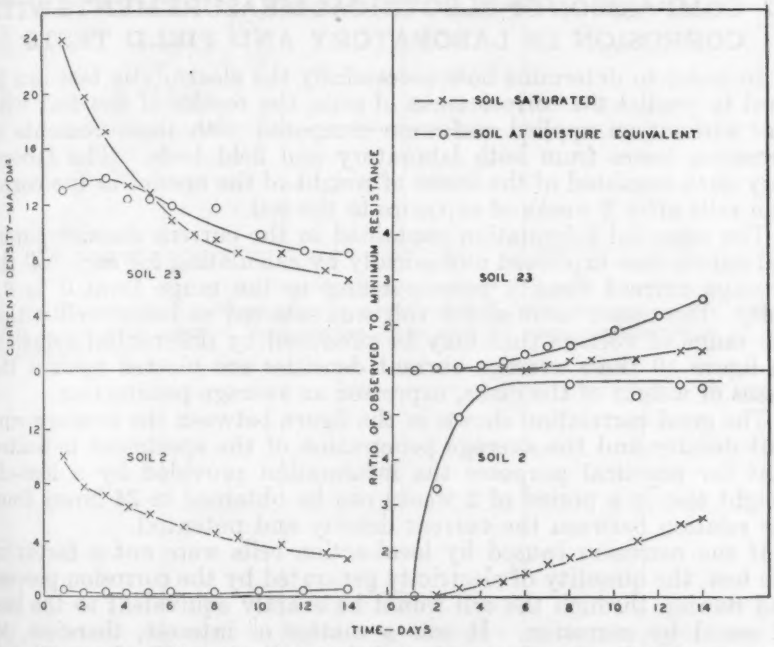

FIGURE 9.—*Effect of moisture content on current density and resistance.*

The explanation for this marked difference in behavior of the two soils is to be found in the formation of a protective carbonate layer in soil 2 at the moisture equivalent. With the soil in the well aerated condition that exists at the moisture equivalent, production of carbon dioxide by bacterial activity proceeds rapidly. The reaction between dissolved carbon dioxide and the calcium and magnesium ions concentrated at the cathode under the influence of the current, in the presence of the hydroxyl ions produced at the cathode, causes the formation of a difficultly soluble protective layer. The increased resistance of this layer produces the marked diminution in current shown in the figure. No such deposit was possible in soil 23, in which ions capable of forming protective deposits are practically absent.

This explanation was confirmed by an experiment in which cells containing these and similar soils in a saturated condition were exposed to an atmosphere containing 15 percent of carbon dioxide.

Marked reductions in current were noticed within 24 hours in soil 2 and similar soils, but not in soils such as 23.

From the results of the studies just described it is reasonable to infer that, in the absence of large concentrations of soluble salts, the action of calcium and magnesium carbonates in inhibiting corrosion would depend largely on the aeration of the soil. The carbonates of the alkaline earths are probably important factors in limiting the rate of corrosion in porous, well-drained soils, where the production of carbonate films is favored. On the other hand, in heavy, poorly drained soils, where the rate of production of carbon dioxide is necessarily limited, there is little tendency for films to be formed and no reduction in the rate of corrosion is to be expected.

VI. COMPARISON OF ELECTRICAL MEASUREMENTS WITH CORROSION IN LABORATORY AND FIELD TESTS

In order to determine how successfully the electrolytic test can be used to predict the corrosiveness of soils, the results of the test with and without an applied emf were compared with measurements of corrosion losses from both laboratory and field tests. The laboratory data consisted of the losses of weight of the anodes in the corrosion cells after 2 weeks of exposure to the soil.

The essential information contained in the current density-potential curves was expressed numerically by calculating for each soil the average current density corresponding to the range from 0 to 0.3 volt. The upper limit of 0.3 volt was selected as being well within the range of voltage that may be produced by differential aeration. In figure 10 these average current densities are plotted against the losses of weight of the disks, expressed as average penetration.

The good correlation shown in the figure between the average current density and the average penetration of the specimens indicates that for practical purposes the information provided by a loss-of-weight test in a period of 2 weeks can be obtained in 24 hours from the relation between the current density and potential.

If the corrosion caused by local-action cells were not a factor in the test, the quantity of electricity generated by the corrosion process and flowing through the cell would be exactly equivalent to the loss of metal by corrosion. It was a matter of interest, therefore, to compare the average penetration of the specimens with the estimated quantity of electricity produced by the cell over the period of test (fig. 11).

The departure of the relation shown in figure 11 from the theoretical linear relation is to be ascribed to local corrosion at the lower current densities. It is seen that the rate of increase of average penetration per unit of electricity decreases until the quantity of electricity reaches about 0.2 ampere-hour, after which the average penetration is roughly proportional to the quantity of electricity. This relation simply means that at the lower current densities,[14] the current flowing through the cells is but a fractional part of the total current associated with corrosion. It follows, therefore, that at the lower current densities much of the nominal anode surface actually acts as a cathode, and the corrosion circuits are confined largely to the disk. As the current density increases an increasingly larger fraction of the disk becomes anodic until at some relatively high current density, prac-

[14] Since the time and size of specimen is the same for all soils current density may be considered as proportional to quantity of electricity.

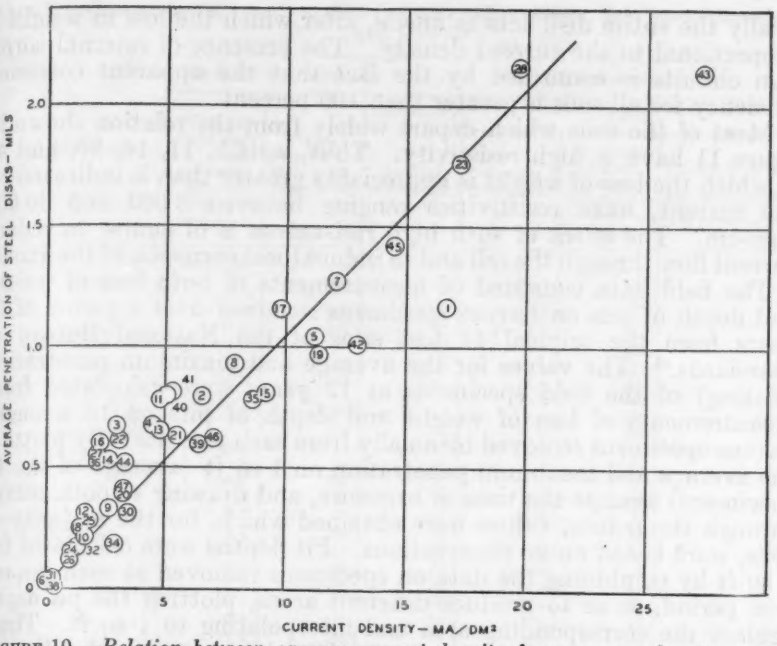

FIGURE 10.—*Relation between average current density from current density potential curves with applied electromotive force and the average penetration of test specimens.*

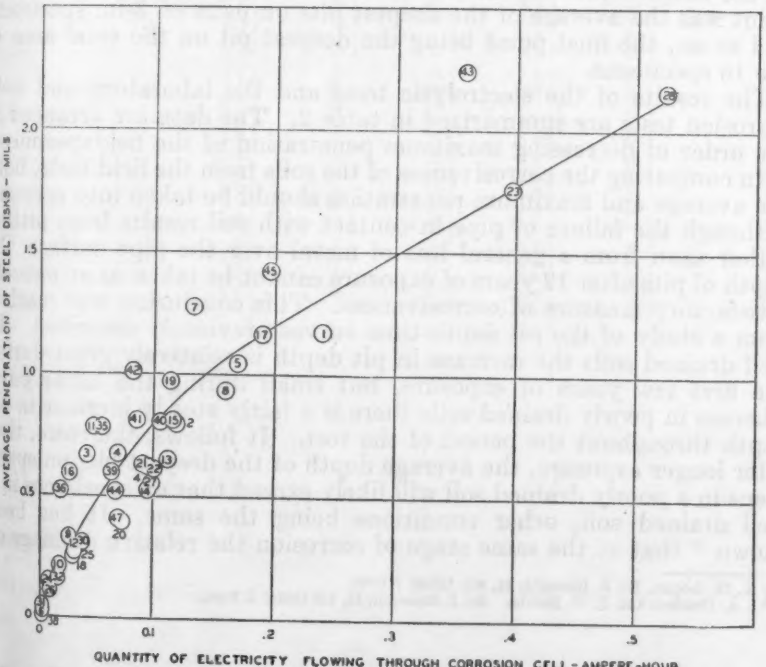

FIGURE 11.—*Relation between the quantity of electricity and the average penetration of the test specimens.*

tically the entire disk acts as anode, after which the loss in weight is proportional to the current density. The presence of internal corrosion circuits is confirmed by the fact that the apparent corrosion efficiency for all soils is greater than 100 percent.

Most of the soils which depart widely from the relation shown in figure 11 have a high resistivity. Thus, soils 3, 11, 16, 36, and 42 in which the loss of weight is appreciably greater than is indicated by the current, have resistivities ranging between 8 000 and 30 000 ohm-cm. The effect of such high resistances is of course to reduce current flow through the cell and to induce local corrosion of the anode.

The field data consisted of measurements of both loss of weight and depth of pits on ferrous specimens removed over a period of 12 years from the original 47 test sites of the National Bureau of Standards.[15] The values for the average and maximum penetration (pitting) of the field specimens at 12 years were calculated from measurements of loss of weight and depth of pits on 16 wrought ferrous specimens removed biennially from each test site. By plotting the average and maximum penetration on 1 sq ft (average of the 16 specimens) against the time of exposure, and drawing smooth curves through the points, values were obtained which, for the majority of soils, were based on 96 observations. Pit depths were calculated for 1 sq ft by combining the data on specimens removed at each inspection period, so as to produce different areas, plotting the pit depth against the corresponding area and interpolating to 1 sq ft. Thus, the first point on the curve was obtained by averaging the deepest pits on equivalent 3-in. specimens, that is, it was the average depth of the deepest pits on the area of one 3-in. specimen. The second point was the average of the deepest pits on pairs of 3-in. specimens and so on, the final point being the deepest pit on the total area of the 16 specimens.

The results of the electrolytic tests and the laboratory and field corrosion tests are summarized in table 2. The data are arranged in the order of decreasing maximum penetration of the field specimens.

In comparing the corrosiveness of the soils from the field tests, both the average and maximum penetration should be taken into account. Although the failure of pipe in contact with soil results from pitting rather than from a general loss of metal over the pipe surface, the depth of pits after 12 years of exposure cannot be taken as an entirely satisfactory measure of corrosiveness. This conclusion was reached from a study of the pit depth-time curves previously described. In well drained soils the increase in pit depth is relatively great during the first few years of exposure, but small during the latter part; whereas in poorly drained soils there is a fairly steady increase in pit depth throughout the period of the test. It follows, therefore, that after longer exposure, the average depth of the deepest pits on specimens in a poorly drained soil will likely exceed that on specimens in a well drained soil, other conditions being the same. It has been shown [16] that at the same stage of corrosion the relative drainage or

[15] K. H. Logan, BS J. Research **16**, 431 (1936) RP883.
[16] I. A. Denison and R. B. Hobbs. BS J. Research **13**, 125 (1934) RP696.

TABLE 2.—*Comparison of results of electrical tests with corrosion data from laboratory and field tests*

Soil	Electrical test results		Corrosion test results			
			Laboratory	Field		
	With applied emf. Average current density between 0 and 0.3 v	Without applied emf. Quantity of electricity	Average penetration in 2 wk	Average penetration in 12 yr	Estimated average maximum penetration in 12 yr on 1 sq ft	Pitting factor at 12 yr: max penetration / avg penetration
	ma/dm²	ma-hr	mils	mils	mils	
28	19.7	525	2.16	29.6	229	7.7
29	(c) 21.0	(a)	(a)	27.0	195	7.2
23	17.2	397	1.76	32.8	191	5.8
45	14.5	197	1.42	(b) 19.5	167	8.6
14	4.4	88	.53	7.4	138	18.7
43	27.3	358	2.24	24.5	132	5.4
42	13.0	83	1.01	18.4	120	6.5
33	(c) 20.2	(a)	(a)	20.7	119	5.8
6	7.9	160	.93	8.0	105	13.1
40	5.1	106	.80	11.8	105	8.9
37	19.2	(a)	(a)	14.0	100	7.1
46	7.1	86	.62	7.1	100	14.0
1	16.7	240	1.17	15.2	98	6.4
11	4.8	49	.78	3.1	93	30.0
4	9.5	70	.67	10.6	90	8.5
16	3.4	28	.60	11.7	87	7.4
41	5.3	87	.81	9.2	85	9.2
3	3.0	43	.67	6.9	85	12.3
44	3.4	69	.52	3.8	84	22.1
39	6.4	65	.60	8.6	83	9.7
15	9.2	117	.81	12.6	78	6.2
10	11.4	115	.97	5.2	78	15.0
22	4.2	101	.61	11.5	76	6.6
12	1.7	33	.31	5.7	76	13.3
5	11.2	171	1.05	10.6	75	7.1
27	2.2	99	.55	11.5	73	6.4
2	6.6	120	.80	9.4	72	7.7
20	3.3	75	.39	9.2	71	7.7
34	3.0	(a)	(a)	6.9	66	9.6
10	1.7	19	.21	7.4	64	8.7
9	2.7	28	.33	7.4	60	8.1
18	1.5	31	.25	4.9	59	12.0
36	2.2	20	.52	4.1	56	13.7
25	1.9	33	.27	5.1	55	10.8
32	1.3	17	.16	5.5	55	10.0
7	12.1	133	1.28	7.8	54	6.9
30	3.5	40	.31	8.8	54	6.2
26	1.1	9	.12	6.0	54	9.0
35	8.7	57	.78	3.2	53	16.6
17	9.8	190	1.16	14.8	49	3.3
31	.3	2	.04	4.2	45	10.7
47	3.3	71	.41	4.9	39	8.0
38	.4	1	.01	3.8	39	10.3
24	1.1	8	.15	2.1	26	12.4
6	.0	2	.03	1.8	25	13.9

[a] Cell had no definite polarity.
[b] Average penetration in 10 years.
[c] Cathode bare.

permeability of a soil is indicated by the pitting factor, which is the ratio of maximum penetration to average penetration. A low pitting factor is indicative of poor drainage, whereas a high factor is indicative of good drainage conditions. Consequently, a given depth of pit associated with a low average penetration (low pitting factor) should be given greater weight than when the same pit depth is associated with high average penetration (high pitting factor).

The foregoing discussion of certain features of underground corrosion helps to explain several of the inconsistencies between the field and laboratory data shown in table 2. For example, the maximum depth of pit on the specimens from soil 17 is but 49 mils, although according to the laboratory tests this soil would be classed as definitely corrosive. However, the high average penetration of 14.8 mils is consistent with the results of the laboratory tests. As indicated by the low pitting factor of 3.3, this soil is poorly drained, which is a condition favorable to deterioration of ferrous metals. The corrosiveness of the soil is further supported by its extreme acidity, the pH value being 4.5 and the total acidity 19.1 mg-eq. On the other hand, soils 11 and 44 are probably less corrosive than would be indicated by the pit depths of 93 and 84 mils, respectively. The low average penetration of 3.1 and 3.8 mils and the high pitting factors of 30.0 and 22.2, are consistent with the fact that these test sites are well drained and that the pits are not likely to deepen greatly with time.

Soil 7 is a very acid soil which, for some reason peculiar to the test site, does not appear from the field test to be corrosive. In view of its extreme acidity (pH 4.4 and total acidity 29.8 mg-eq) it is probable that, under slightly different conditions of aeration or drainage, serious corrosion might be experienced in this soil. The slight corrosiveness of soil 35 in the field tests is probably due to the low rainfall and consequent dryness of the soil. The average annual precipitation at this site in Los Angeles was but 11.75 in. during the 10-year period of the test. The marked depth of pitting of specimens in soil 14 is probably due to some peculiar condition of the test site rather than to the soil in contact with the specimens.

If the results of the laboratory and field tests shown in table 2 are compared with the properties of the soils given in table 1, certain effects of chemical composition on the rate of corrosion may be noted. Thus the most corrosive soils are with few exceptions either very acid soils or soils which contain large quantities of salts, chiefly of sodium and potassium. The moderately corrosive soils, which produce a maximum penetration between 75 and 105 mils, are either moderately acid or contain appreciable concentrations of soluble material. Soils 8, 15, 2, and 27 are of interest because they are only moderately corrosive, although they contain fairly high concentrations of soluble material. However, it will be noted from the analyses that the equivalents of calcium and magnesium ions in these soils either exceed those of sodium and potassium or at least form a relatively large part of the total bases. The moderate corrosivenes of soil 8 suggests that fairly high concentrations of calcium and magnesium ions, when present largely as sulfates, are not necessarily corrosive in the presence of solid calcium carbonate under conditions of reasonably good drainage. With regard to the following alkaline soils, 27, 47, 20, 30, 25, 18, 32, and 26, it should be noted that not only

is the soluble material low in amount but that the ions of calcium and magnesium predominate over the alkalies.

In figure 12 the data from the laboratory corrosion test (column 5, table 2) are shown plotted against the average depth of the maximum pit on the field specimens after 12 years (column 7). The scattering of the points should be attributed largely to the fact that the pit-depth-time curves do not all have the same shape, but show a marked tendency to intersect after long periods. As previously stated, the tendency for the rate of pitting to decrease with time is greatest in

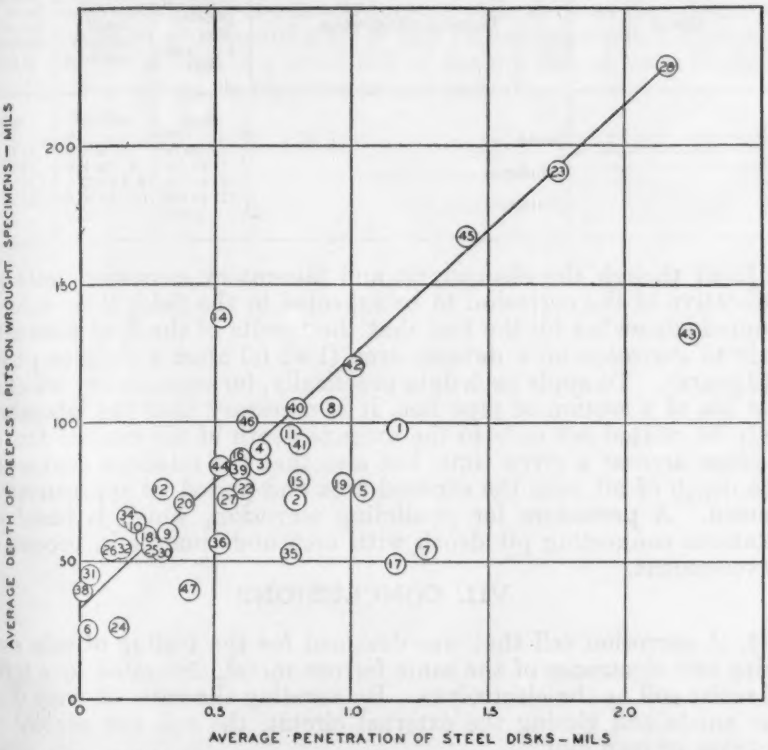

FIGURE 12.—*Relation between the maximum penetration of field specimens at 12 years and the average penetration of test specimens.*

well drained soils and least in poorly drained soils. The points which deviate widely from the trend line, such as those for soils 1, 7, 17, 43, and 47 are all more or less poorly drained. After greater periods of time it is reasonable to predict that these points will be nearer the curve than they are after 12 years.

In order to facilitate the practical application of the corrosion test it is desirable to set limits of current density and average penetration which will indicate the range of pit depth to be expected in practice in soils of unknown corrosiveness. Table 3 has been prepared by arbitrarily dividing the soils tested into groups and selecting for each group limiting values of (1) pit depth on 1 sq. ft. at 12 years; (2) average current density corresponding to the range of 0 to 0.3 volt;

and (3) average penetration of the test specimens. Since the relative corrosiveness of the different groups may not be readily appreciated from the measurements of pit depth on 1 sq ft, qualitative terms characterizing the degree of corrosiveness of the groups are included in the table.

TABLE 3.—*Classification of soils on basis of corrosiveness as indicated by field and laboratory tests*

Group	Degree of corrosiveness	Estimated maximum penetration on 1 sq ft at 12 yr	Average current density between 0 and 0.3 v	Average penetration of test specimens in 2 wk
		mils	ma/dm²	mils
I	Mild	<40	0	>0.1
II		41 to 70	.1 to 4.0	.11 to 0.45
III	Moderate	71 to 100	4.1 to 8.0	.46 to 0.80
IV		101 to 130	8.1 to 12.0	.81 to 1.15
V	Extreme	131 to 160	12.1 to 16.0	1.16 to 1.50
VI		>161	>16.1	>1.50

Even though the electrolytic and laboratory corrosion tests are indicative of the corrosion to be expected in the field, their value is limited somewhat by the fact that the results of the field tests refer only to corrosion on a definite area (1 sq ft) after a definite period (12 years). To apply such data practically, for example in predicting the life of a section of pipe line, it is necessary that the laboratory data be related not only to the average depth of the deepest pits on a given area at a given time, but also that the relations connecting the depth of pit with the exposed area and period be approximately known. A procedure for predicting corrosion, which is based on relations connecting pit depth with area and time, is in process of development.

VII. CONCLUSIONS

1. A corrosion cell that was designed for the testing of soils contains two electrodes of the same ferrous metal, separated by a layer of moist soil as the electrolyte. By aerating the cathode more than the anode and closing the external circuit, the cell was enabled to develop its own emf.

2. The quantity of electricity developed by the cell over a 2-weeks' period is approximately proportional to the loss of weight of the anode and to corrosion losses in field tests.

3. The corrosion test may be accelerated by the use of an external emf. From the relation between current density and the voltage impressed across the cell, corrected for IR drop, the relative corrosiveness of soils can be predicted.

4. The time curves of voltage, current and resistance of corrosion cells that operated with only the emf associated with corrosion, were influenced by the physical and chemical properties of soils.

5. The chief factors that induce corrosion in soils are high concentrations of soluble salts, especially those of the alkali metals; and high acidity. Both factors tend to increase the solubility of the hydroxides of iron and to prevent the formation of protective layers of corrosion products.

6. Corrosion is relatively slight, except under conditions of poor drainage, in soils in which the content of bicarbonate in a water extract of the soil is equivalent to the sum of the calcium and magnesium ions. Well aerated soils, in which the hydroxides of iron are precipitated in immediate contact with the corroding surface, are usually noncorrosive.

7. The results of a laboratory test on a soil were correlated with the loss in weight and the depth of the deepest pit on 1 sq ft of ferrous materials exposed to that soil for 12 years.

8. A laboratory test of corrosiveness of soils, such as that described in this paper, is an essential part of any rational procedure for calculating the life of pipe in a given soil or the number of leaks likely to develop on a section of pipe line in any period.

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THERMAL CONTROL IN MINIMUM-DEVIATION REFRACTOMETRY AND TEMPERATURE COEFFICIENTS FOR A MEDIUM FLINT GLASS

By Leroy W. Tilton

ABSTRACT

Constructional details are given for a constant-temperature housing for minimum-deviation measurements on a spectrometer, and the operational procedure is described. Provision is made for mounting and properly adjusting the prism in a temperature-controlled bath of stirred air contained in a water-jacketed cylinder provided with plane-parallel windows that are adjustable for use over a wide range of prism angles and refractive media. Typical temperature coefficients of refractivity are given for a medium flint glass.

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INTRODUCTION

Certain requirements of sixth-decimal place refractometry have been discussed by the writer in former papers,[1] and some indications have been given concerning procedures that should be followed in using a spectrometer and the minimum-deviation method for precise and accurate determinations of refractive index. Of the procedures outlined, the most difficult from the experimental standpoint is the design, construction, and use of an adequate prism housing [2] for control of both air and prism temperatures while minimum deviations are observed.

Aside from the obvious advantages of such a housing for an accurate determination of refractivity at any given temperature, its use is desirable in determining precise values for temperature coefficients of index, not only at ordinary room temperatures but at others somewhat different therefrom. This is particularly so since interferometric methods [3] of determining such thermo-optical properties

[1] BS J. Research **2**, 909-930 (1929) RP64; **6**, 59-76 (1931) RP262; **11**, 25-57 (1933) RP575; J. Research NBS **14**, 393-418 (1935) RP776.

[2] See brief discussion on p. 919 and 920 of first citation in footnote 1. These difficulties influenced J. F. Eckman when he rejected minimum deviation and designed his constant-deviation refractometer. See p. 14 of Rec. trav. chim. **13** (1894).

[3] See, for example, C. G. Peters, BS Sci. Pap. **20**, 635-659 (1926) S521.

are usually unreliable at and near room temperatures, on account of what is sometimes called the "starting effect".[4] Also, a temperature-control housing is desirable because only a limited temperature range is available in using a constant-temperature room.

In the literature, however, a certain scepticism is sometimes expressed regarding the advisability of depending upon a housing, rather than upon a constant-temperature room, when determining temperature coefficients of index. This paper is consequently written not only to describe a successful housing suitable for general spectrometric use, but also to give in detail results which indicate that its use is satisfactory.

II. CONSTANT-TEMPERATURE PRISM HOUSING

The prism housing used by J. Macé de Lépinay[5] is probably sufficiently characteristic of the best previous efforts to provide minimum-deviation housings for work on prisms of solid media. His prism was immersed in air that in turn was surrounded on sides and top by an insulated and water-jacketed box or cover. Fixed lateral openings for the entrant and emergent light were closed with thick wooden stoppers except during the actual measurements.

More elaborate housings have been used by W. H. Perkin,[6] also by E. E. Hall and A. R. Payne,[7] for work on liquids contained in a hollow prism, but even in these the housing windows were opaque and therefore were opened during measurements. G. P. Baxter, L. L. Burgess, and H. W. Daut[8] avoided this undesirable procedure by having the telescope and collimator tubes extend into the air bath and by providing adjustable shutters which made a tight fit with these tubes. Moreover, they devised a separate mounting to avoid placing the extra weight on the spectrometer. Even this design, however, was for special rather than for general use, just as had been the case with all previous housings for minimum-deviation measurements.

1. GENERAL DESCRIPTION

The prism housing that has been used for several years in this laboratory was designed by F. A. Case of the Optical Instruments Section and built in the Bureau's Instrument Shop. It consists (see figs. 1 to 4, inclusive), primarily of two vertical concentric hollow cylinders of brass each containing a circular window of glass. The inner cylinder and its integrally connected top are double walled to form a water jacket. The outer cylinder or single-walled sleeve fits closely and rotates around the double walls of the inner cylinder. This whole superstructure rotates on and is readily removable from low vertical walls at the periphery of a water-jacketed base which is firmly attached to the prism table of the spectrometer.

Lateral openings are, of course, necessary in the walls of the inner cylinder and also in the sleeve in order to permit the simultaneous

[4] See C. Cuthbertson, Trans. Roy. Soc. (London) [A] **204**, 331 (1905). This starting effect consists of irregular fringe shifts which occur before the temperature gradients within the interferometer have assumed the values which correspond to a steady heating rate. Even if both heating and cooling are successively employed in a continuous and regular series of observations, including temperatures both higher and lower than those of the room, some degree of undesirable fringe shift must occur at and near room temperatures because of reversals which must take place in the temperature gradients.

[5] Ann. chim. phys. [7] **5**, 216–232 (1895).

[6] J. Chem. Soc. **61**, 287–290 (1892).

[7] Phys. Rev. [2] **20**, 249–258 (1922).

[8] J. Am. Chem. Soc. **33**, 893–901 (1911).

use of both windows, one for the entrant and one for the emergent light. These lateral openings are sufficiently wide to permit a clear aperture of at least 2 cm in width over a range of deviations from 17 to 81 degrees of arc. Clamps and slow-motion screws are provided for adequate orientation adjustments; first, of the inner cylinder and window with respect to the prism and, second, of the rotating sleeve and its window with respect to the inner cylinder and the first window. These clamps are designed to operate at all positions around the circumference of the housing. The whole metal exterior of the prism housing is covered with felt and asbestos.

Secured to the upper floor of the water-jacketed base are two prism slides that travel in superimposed ways at right angles with each other. These slides are actuated by slow-motion screws that are controlled from without the prism housing. Two circular wells in the double-walled top permit the insertion of thermometers to desired depths in the air bath. Through a third opening in the center of the top an air stirrer is inserted. This consists of a small vertical shaft carrying two sets of propeller blades. The upper set, outside the housing, is driven by a compressed-air jet; the lower stirs the air bath within the housing. This device gives adequate stirring with a minimum of weight, volume, and vibration as compared with a stirrer operated by other means.

The window cells are hinged at their tops on horizontal axes and are fastened at the base by adjusting screws. These screws turn the windows through a vertical angle of a few degrees and thus permit autocollimated reflections from the windows to be properly returned to, or entirely excluded from, the field of view of the telescope. The window frames are fitted with rubber sills to give effective closing for a range of adjusted orientations about the horizontal hinges of the cells.

The windows are of borosilicate crown glass of good quality. Their surfaces are flat within $1/4\lambda$ over their clear 49-mm aperture. As plane parallels their errors are in each case less than 1 second of arc. Moreover, as prisms they are mounted in their cells with the refracting edges in a horizontal plane in such manner that at one window the light beam is depressed and at the other window elevated through angles of approximately 0.5 seconds but with entirely negligible lateral deviation. Care was used when mounting the windows to avoid deforming them by the pressure of their retaining rings. Tests on prism-angle measurement, with and without the housing, show agreements within a few tenths of a second with no systematic effect arising from the use of the housing.

2. CONSTRUCTIONAL DETAILS

Some details of construction of the prism housing are evident from the accompanying illustrative figures, which, however, are partly diagrammatic. Figure 1 is a sectional elevation of the complete housing showing how the lower clamp and screw serve to orient the superstructure with respect to the base, and also how the upper clamp and screw rotates the single-walled sleeve around the double inner cylinder. These screws are so designed that in each case the knurled head extends toward the observer's station at the times when a particular screw should be used. This automatically prevents the

inadvertent orientation of the outer window by a procedure that would vitiate the previous adjustment of the other window.

Figure 2 is a sectional plan at the level of the window centers. This shows how the window cells are attached to and carried by the rotating cylinders and also, in connection with figure 1, how the upper prism slide is controlled from the exterior irrespective of the lateral shifts which may occur because it is mounted on the lower slide. For this purpose the nut k, which travels on the screw l, engages at all times with a slot m in the roof of the recessed cavity under the upper slide. The manipulation of these slides from without the housing is especially advantageous because delays in attaining

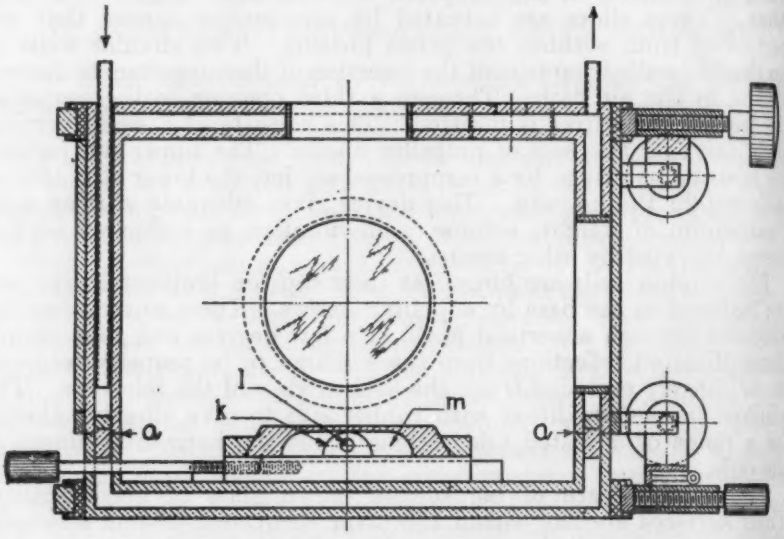

FIGURE 1.—*Sectional elevation of prism housing, showing junction between base and superstructure at* aa.

temperature equilibrium would result if, after angle measurement, the housing were opened to translate [9] the prism to the deviation position.

Figure 3 is a top view of the superstructure. The central well in the top is large in order to accommodate a long-stem mercury thermometer, if such is used, in a hollow prism during its requisite translational adjustment on the slides for either angle or deviation measurement. In such a case the thermometer stem extends through a thick pad of felt which effectually closes the opening and the air stirrer (with its similar pad of felt) is transferred to one of the thermometer wells. These smaller wells at each side of the central well are threaded to receive the protective metal casings in which are housed the mercury thermometers used for determining the air-bath temperatures.

Figure 4 shows how the glass windows are mounted in their cells and secured by retaining rings q. Orientation and adjustment about their horizontal axes or hinges is provided by the friction thumb screws r.

[9] See p. 31 and 35 of BS J. Research 11 (1933) RP575.

The prism inlet and outlet connections, s and t, shown in figure 2, provide for inserting the intimate jacketing system of a hollow prism that is used when measuring the refractive indices of liquids. At other times they are short-circuited by a semicircular connection or by a radiating coil of a few turns of copper tubing. Under various working conditions the sequence of flow through the jacketing connections (indicated in only one particular manner on these diagrams) is varied to secure greater uniformity of temperature or a decreased lag in response to the action of the thermoregulator.

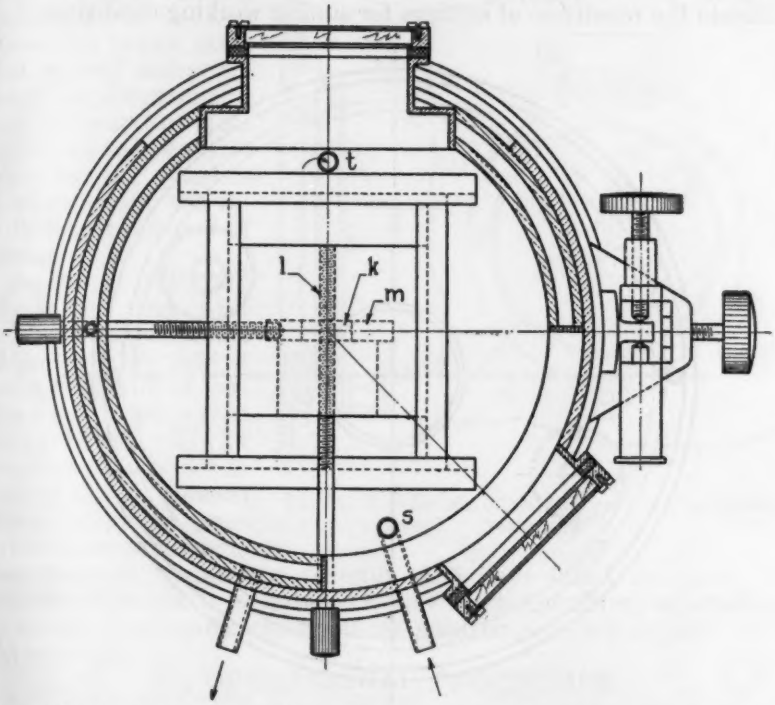

FIGURE 2.—*Sectional plan of prism housing at level of window centers and plan view of prism slides.*

3. JACKETING CIRCUIT

On a shelf, directly above the spectrometer but suspended from the ceiling, are located a motor, a rotary pump, and a mixing or conditioning chamber which contains a thermoregulator of the usual bulb and U-tube type with toluol as the expansive medium and with a movable platinum wire which makes contact with mercury in a capillary tube to provide for fine adjustment. For settings at widely different temperatures it is necessary, however, to vary the amount of toluol in the bulb by means of a glass plunger which separates the effective bulb from a reservoir. A useful feature, which has been tried with some success for rapid and fairly precise gross adjustments of this kind, is the attachment of a metal bellows to the expansion bulb in order that the volume may be varied by a screw that carries a graduated disk.

Three fixed rates of heating are provided by leads to resistance coils in the walls of the mixing chamber, and a lamp operated by current through a relay is partially immersed in the tempering bath to constitute the variable heating element. A constant rate of cooling is effected by means of a continuous flow of tap water from a constant-head storage tank through a coil surrounded by melting ice. This cold water traverses a coil immersed directly in the tempering bath of the jacketing fluid within the mixing chamber and thence passes to the sink. Rate of flow in this cooling circuit is regulated by a cock provided with a long pointer that moves over a graduated arc to facilitate the repetition of settings for similar working conditions.

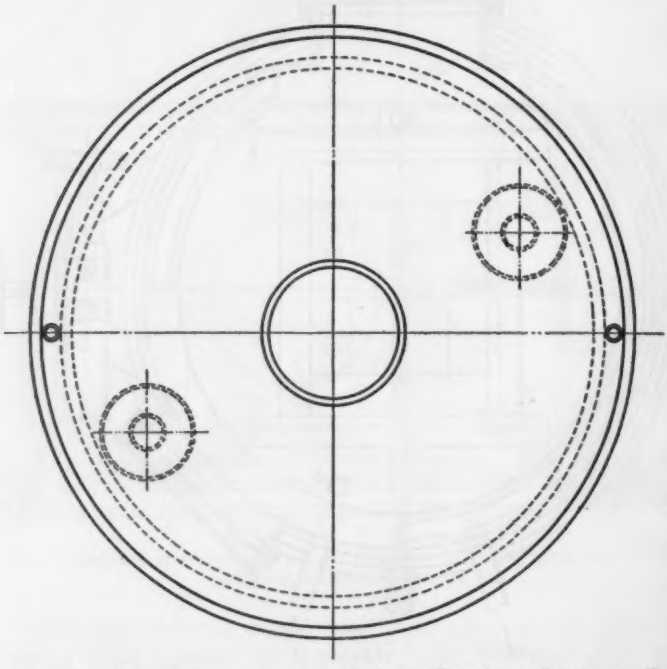

FIGURE 3.—*Top view of superstructure of prism housing, showing wells for air stirrer and thermometers, also inlet and outlet of water jacket.*

Through a series of copper pipes and rubber hose connections the jacketing fluid follows a closed circuit, as diagrammed in figure 5, which includes pump, mixing chamber, the prism-housing base, and the superstructure of the housing. The system is designed to operate between the approximate limits 0 and 60° C. For temperatures at and near 0° C it is, of course, necessary to use some antifreeze solution in the jacketing circuit and to replace tap-water cooling by a more direct arrangement with a portion of the jacketing fluid flowing through a by-pass which includes a coil immersed in a freezing mixture.

4. SUSPENSION AND COUNTERBALANCE

To avoid undesirable weight on the prism table and on the spectrometer a piano-wire suspension with counterweight was devised with a pulley at the ceiling directly over the spectrometer axis. A

three-point wire suspension, with turnbuckles in two of the wires, was attached to the superstructure of the housing, and to further lessen torque a chain of three circular steel rings was used just above the triple junction which is approximately 18 inches above the housing top. The counterweight consists of a lead-filled brass tube perforated longitudinally to slide freely for a distance of about 15 inches on a vertical guide rod which is securely attached to the ceiling. The weights of all hose connections to the prism housing are likewise carried by this device.

A horizontally sliding shelf about 13 inches above the prism table (but entirely independent of the spectrometer and its supporting table) receives the prism housing when it is elevated for the installation or removal of a prism.

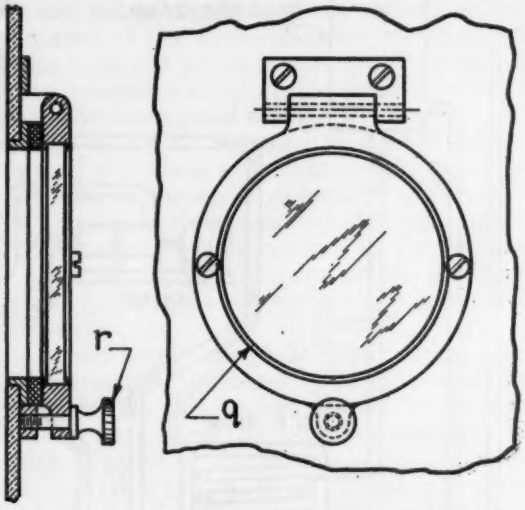

FIGURE 4.—*Details of window cells and adjustable mounting.*

Experience in the use of this housing, and tests of the adjustments of the spectrometer which are made at various times, indicate that the residual weight which rests on the prism table of the instrument does not cause any appreciable errors in angle measurements. Moreover, careful tests have failed to show that appreciable torque is introduced even when the arbitrary orientations in azimuth materially exceed those occurring during regular use of the housing.

III. OPERATIONAL PROCEDURE

In determining an index of refraction, using this prism housing, the additional operations (as compared with procedure otherwise followed) are briefly named as (1) the adjustment of the thermoregulator and its system, and (2) the proper orientations of the windows of the housing. The time required is essentially that which is necessary in establishing a constant thermal condition in the apparatus, and most manipulations of the prism and its housing are easily made while waiting for equilibrium conditions.

1. REFRACTING-ANGLE MEASUREMENTS (BY AUTOCOLLIMATION)

It is advisable to make refracting-angle measurements before deviation measurements because the thermal requirements are probably somewhat less exacting. Immediately after starting the regulatory system, the prism is mounted [10] on a suitable glass slab on the upper

[10] Wax in very small quantities is very satisfactory for general use in attaching prisms to the brass slide or to an intermediate block of glass or of asbestos plate. Soft pitch has also been used at temperatures above 40° C. An auxiliary prism holder, provided with leveling screws and a platform adjustable in height, would be a great convenience, and, moreover, it would obviate a slight tilting of the whole housing that otherwise occurs in the process of leveling.

prism slide and the prism table is approximately leveled. Next, the housing is lowered and the windows oriented by hand to approximately the angle between the prism faces, using for these orientations certain fiducial marks or scales on the side of the housing. By means of the prism-slide controls the prism is then properly "centered" [11] for angle measurement while the observer views the exit pupil of the

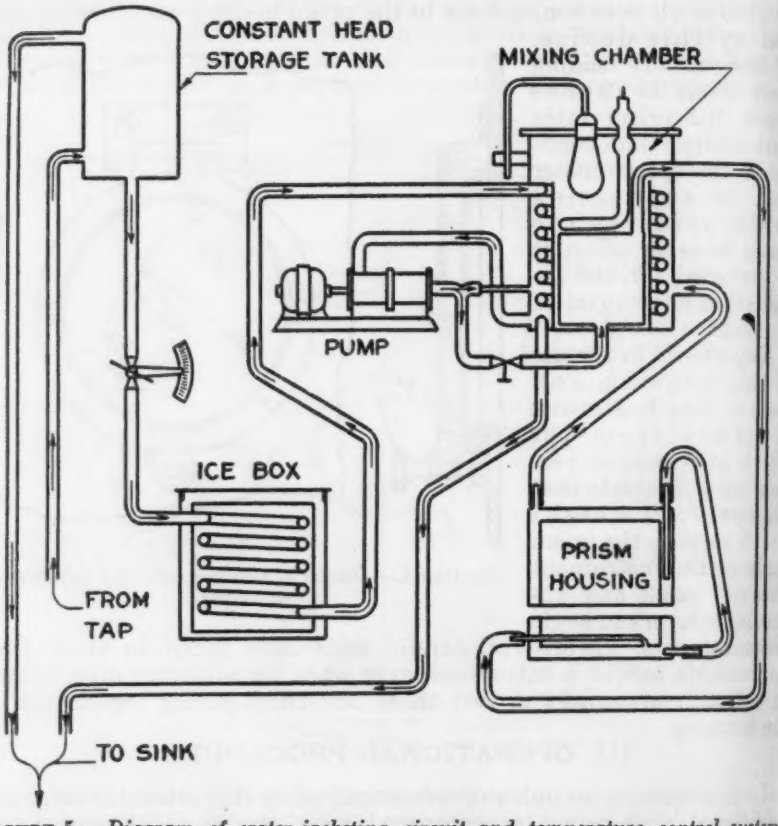

FIGURE 5.—*Diagram of water-jacketing circuit and temperature control system.*

This figure is not drawn to scale. The hose connections from mixing chamber to prism housing are long and flexible and their weight, like that of the housing, is largely supported by a counterweight and wire over a pulley attached to the ceiling.

autocollimator with an auxiliary eyepiece or magnifier. After this, using autocollimation, the "fixed window" of the inner cylinder is adjusted (with the lower clamp and screw) until it is parallel to one of the prism faces and then (by the upper clamp and screw) the "movable window" of the sleeve is brought parallel to the second face of the prism. Usually the windows must be adjusted slightly about their horizontal (hinge) axes to permit them to act as useful reflectors and, finally, they are slightly depressed so reflections therefrom do not interfere with the refracting-angle measurements, which are made only after an accurate leveling of the prism.

[11] See p. 31 of third citation in footnote 1, p. 389.

2. MINIMUM-DEVIATION MEASUREMENTS

After refracting-angle measurements both clamps are loosened and the windows set by hand to the approximate angle which (from experience) is estimated as suitable for double-deviation measurements. The superstructure of the housing is oriented by hand about 180 degrees on its base and the whole prism table, prism, and housing is so oriented that the prism is approximately in the position for minimum deviation to the observer's left.[12] Then the superstructure is so oriented on its base that the fixed window is approximately normal to the emergent rays. With the aid of autocollimated reflections and using the slide controls the apex of the prism should next be moved toward the spectrometer axis until the prism is uniquely [13] placed for deviations, and after that a normal setting of the fixed window is accurately obtained by the lower clamp and screw.

Both prism table and telescope are then turned to their respective positions for right-hand deviation and the upper clamp and screw are used for securing a normal setting of the movable window with respect to the emergent light. On account of the symmetry of the minimum-deviation position the fixed window is now normal to the incident rays from the collimator and, also, when the orientations are again changed for left-hand deviation, the movable window will necessarily be normal to the collimated beam.

The maintenance of the prism level during the prism translations and the housing orientations can be checked by a glance at the (deviated) image of the slit which for this purpose should have a horizontal fiducial wire or mark. As a check on several important adjustments, the (magnified) exit pupil of the telescope should be examined from the right- as well as from the left-hand deviation position. Both examinations should show coincidence, at the prism image center, of images of vertical wires [14] that should be mounted at each of the objectives.

Concerning the above mentioned details of operation it should be remembered that some, such as the proper translations of the prism, must be executed irrespective of the use of a prism housing. Others, such as the normal settings of the windows, do not require really precise adjustments. Refraction at an interface between air at different temperatures is the only error to be eliminated. Assuming the unfavorable condition with error of like sign at each window, it is found that an angular tolerance for one window, corresponding to $\pm 1 \times 10^{-6}$ as the permissible error in refractive index, may be written as

$$T_w = \frac{T_{2D}}{4\Delta\mu},$$

[12] An observer standing somewhat to the left of the instrument and viewing through the prism a deviated image of the collimator slit can, by hand and unaided eye, approximately orient the prism for minimum deviation. Almost at the same time he can, in any well-lighted room, adjust the fixed window so that it is approximately normal to an emergent ray by simply viewing the image of his eye as reflected by the glass of that window.

[13] See p. 31 and 35 of third citation in footnote 1, p. 389. If the prism is symmetrically placed on the upper slide, and if it has been properly centered for angle measurement, then only the upper slide need be used in translating the prism from the angle position to that for deviation. Should examinations of the exit pupil of the telescope shown on coincidence of images of the vertically centered threads at the objectives, then such coincidence must be secured by using the screw that controls lateral or transverse translation of the prism.

[14] See footnote 13, also the writer's remarks on proper tabling of prisms, BS J. Research 11, 39 (1933) RP575.

where T_{2D} is a tolerance in (double) minimum-deviation measurement that has already been evaluated [15] and $\Delta\mu$ for air cannot exceed 0.00004 for use of the housing in the laboratory at controlled housing temperatures in the range 0 to 60° C. For prisms with refracting angles of 30 degrees the tolerance in normality of each window adjustment is found to be about 0.4 degree while for 60-degree prisms the tolerance is from 2½ to 5 times as large. If the housing windows are oriented for deviation while observing for some wave length near the midrange of the frequencies that are to be used, then for work over the whole visible spectrum it is unnecessary to readjust the windows except possibly when working with media of fairly high dispersive properties at extremes of the above-mentioned temperature range.

Thus, it seems appropriate to emphasize that, in general, the operations incident to the use of this prism housing, and also most other adjustments of the prism, can be performed while waiting for satisfactorily constant thermal conditions for refractive-index measurements. To give an idea of the rate of working possible in determining index of refraction as outlined here it may be added that in a certain instance 48 determinations of refracting angle and 52 determinations of minimum deviation on a total of 12 prisms were made (by a single observer) in 42 working hours. Each of these 100 determinations consisted of angle measurements for each of three positions of the circular scale of the spectrometer, together with adequate thermometer, barometer, and hygrometric readings, all of which were taken by the same observer for use in making reductions to standard conditions.

IV. TYPICAL TEMPERATURE COEFFICIENTS OF REFRACTION AND DISPERSION

The above-described housing has been in general use for several years for precise refractive-index measurements at definite temperatures [16] usually not far removed from those of the room. In order to further test the housing it was used to determine the refractive index and dispersion of a 60-degree prism of "medium flint" optical glass [17] at the temperatures 5, 15, 25, 35, and 45° C. Five wave lengths were used and minimum deviations were in most cases determined six times, using various portions of the spectrometer circle. The prism angle was determined for three circle positions at 15° C and again, in like manner, at 35° C. Temperatures and humidities were determined for the air inside the housing and the barometer was read during all observations. All indices are corrected to refer to dry air at the same temperature as that of the glass and at a pressure of 760 mm of mercury.

[15] See formula 9 and figure 2 on p. 921 and 922 of first citation in footnote 1, p. 389.
[16] See, for example, p. 721 of BS Sci. Pap. 22 (1928), or p. 624 of BS J. Research 3 (1929).
[17] National Bureau of Standards melt 494. The density of the prism is 3.3491 at 25° C. An analysis gave the following composition:

SiO_2	50.55	Na_2O	2.69	Al_2O_3	0.65	CaO	Trace.
PbO	40.14	K_2O	5.93	Fe_2O_3	0.02	MgO	Not detected.

See also, A. Q. Tool and E. E. Hill, J. Soc. Glass Tech. 9, 196 (1925).

TABLE 1.—*Room-temperature variations in optical density of a medium flint optical glass (smoothed values from observed data by the proces*

TABLE 1.—*Room-temperature variations in optical density of a medium flint optical glass (smoothed values from observed data by the process of graduation)*

($n_O - n_S \equiv$observed minus smoothed indices$\times 10^7$)

[$\Delta n \equiv (n_{t2} - n_{t1}) \times 10^7$]

Temperature (°C)	Refractive index (referred to dry air at t°C and pressure of 760 mm of Hg)															Dispersion		
	λ=6562.8 A			λ=5895.9 A			λ=4861.3 A			λ=4358.3 A			λ=4046.6 A			Average $n_O - n_S$	$\frac{n_D - 1}{\nu = n_F - n_C}$	$\nu_O - \nu_S$	$\Delta\nu$ for 1° C
	n_C	$n_O - n_S$	Δn for 1° C	n_{D1}	$n_O - n_S$	Δn for 1° C	n_F	$n_O - n_S$	Δn for 1° C	n_g	$n_O - n_S$	Δn for 1° C	n_h	$n_O - n_S$	Δn for 1° C				
45	1.5858270	0		1.5901003	−1		1.6008151	−1		1.6094637	−1		1.6169217	−13		−3	39.3713	+0.0002	
40			41.6			45.1			54.5			63.5			72.9				−0.00309
35	1.5857854	+10		1.5900552	+9		1.6007606	+1		1.6094002	+1		1.6168488	+13		+7	39.4022	+0.0024	
30			39.9			43.4			52.8			61.8			71.2				−0.00310
25	1.5857455	−3		1.5900118	−7		1.6007078	+2		1.6093384	−4		1.6167776	−13		−5	39.4332	−0.0013	
20			38.2			41.7			51.1			60.1			69.5				−0.00313
15	1.5857073	+5		1.5899701	−4		1.6006567	−3		1.6092783	+5		1.6167081	+24		+5	39.4645	+0.0021	
10			36.5			40.0			49.4			58.4			67.8				−0.00314
5	1.5856708	−2		1.5899301	−1		1.6006073	0		1.6092199	−5		1.6166403	−12		−4	39.4959	−0.0006	

NOTE.—The average observational imprecision evidenced by these data is 6×10^{-7} in measured refractive index.

These data were adjusted by the process of graduation or smoothing, using double differences and assuming that $\Delta^2 n$ for 1° C has a constant value (which is found to be 1.7×10^{-8}), and all results are given in table 1. The average net residuals (observed minus smoothed indices), as tabulated in column 17 for the various temperatures, evidence a freedom from systematic error in temperatures. From this result and from similar evidence in the temperature range 15 to 55° C it is concluded that this constant-temperature prism housing is satisfactory in the range for which it was designed, namely, from 0 to 60° C.

WASHINGTON, July 21, 1936.

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INSPECTION AND TENSILE TESTS OF SOME WORN WIRE ROPES

By Walter H. Fulweiler, Ambrose H. Stang, and Leroy R. Sweetman

ABSTRACT

In cooperation with the Special Research Committee on Wire Rope of the American Society of Mechanical Engineers, the National Bureau of Standards tested 229 specimens taken from 79 worn wire ropes.

The condition and strength of each sample were determined. The strength was estimated using charts prepared by the Roebling Co. It was found that the estimated strength and the actual strength were nearly the same. These data indicate that the strength of worn ropes may be determined with sufficient accuracy for deciding when the rope should be replaced by measuring the length of wear on the outside wires and counting the number of broken wires.

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I. INTRODUCTION

The problem of determining when a wire rope which has been worn or damaged in service should be replaced by a new rope has received an increasing amount of study during recent years. In the past, no data were available by which an inspector could determine from the surface condition the probable strength and the safety of the rope. Consequently, some inspectors condemned a worn rope either when its actual strength was nearly equal to that of a new rope or, a more dangerous but much less frequent practice, allowed a rope to be used after its strength had become so much reduced that it was unsafe.

To study this problem, the American Society of Mechanical Engineers appointed a Special Research Committee on Wire Rope, W. H. Fulweiler, chairman. This committee asked the users of wire ropes to furnish worn specimens for inspection and tensile tests, and also requested information concerning the service to which the ropes had been subjected so that data might be collected which would serve as a guide to inspectors in determining when a worn wire rope should be replaced. The committee decided to have the inspection and tests made at the National Bureau of Standards under the Bureau research associate plan, directed by H. L. Whittemore, chief of the Engineering Mechanics Section, and A. H. Stang, senior engineer. A program outlining the test procedure was approved by the committee. The results of these tests are given in this report.

In the meantime, John A. Roebling's Sons Co., Trenton, N. J., had published in their magazine, Wire Engineering, articles on the strength of worn ropes. Charts were given from which the strength of a worn wire rope can be estimated if the number of broken wires and the amount of wear on the wires are known. The charts were based on the results of inspection and tests of a large number of worn wire ropes. A. J. Morgan, chief engineer, wire rope division of this company, discussed the proposed program with members of the Bureau staff and made many helpful suggestions which were of great assistance in carrying out the committee's program. Through Mr. Morgan, his company kindly permitted these articles and charts to be used in preparing this report.

II. PRELIMINARY TENSILE TESTS OF NEW WIRE ROPES

The use of zinc sockets for holding wire ropes during tensile tests is now established as a satisfactory method, but the preparation of the samples and the casting of the sockets is an expensive and time-consuming process. A method of holding wire ropes in grips has been developed which is less expensive than the socket method. With the grips no preparation of the wire rope before test is necessary except the removal of the lubricant from the outer surface at the ends of the rope. The seizings at the ends of the specimen come outside the grips.

Before proceeding with the tensile tests of the worn wire ropes it was considered desirable to make tensile tests of new wire ropes when holding the ends by these two methods to determine whether the less expensive method—grips—would be satisfactory for testing the worn ropes.

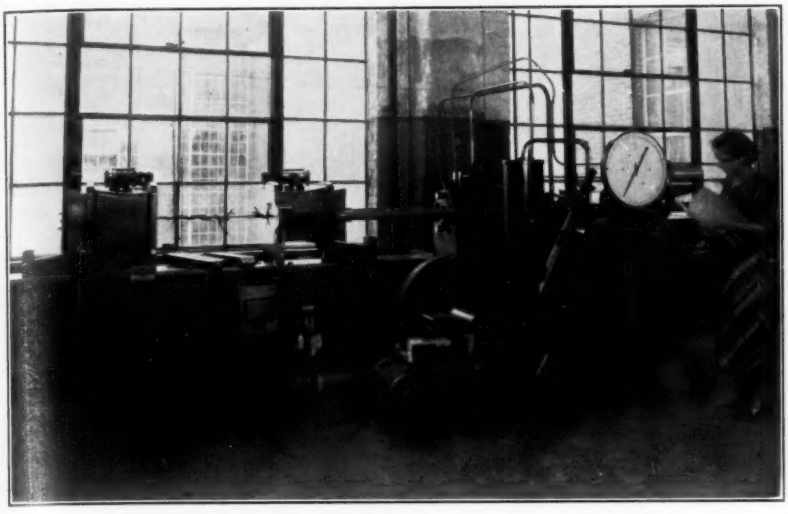

FIGURE 1.—*Horizontal pendulum testing machine, having a capacity of 100,000 pounds, in which the new wire ropes were tested.*

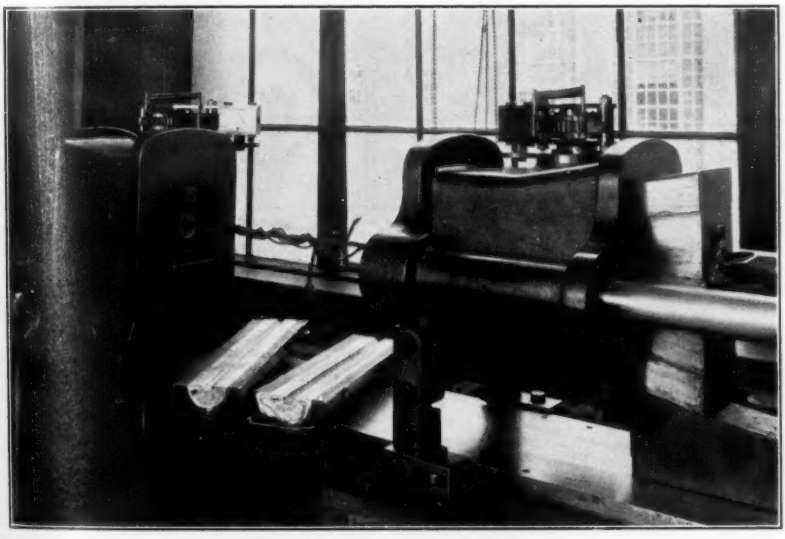

FIGURE 2.—*Grips of the testing machine.*

Two grips lined with cast zinc are shown on the bed of the machine and a wire rope after rupture in other grips in the heads of the machine. As the tensile load on the rope increases, the wedges in the heads move inward, increasing the compressive forces on the ends of the rope. The outside wires of the rope are imbedded in the zinc lining.

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One hundred and thirty foot lengths of both ⅝ and 1-inch diameter new wire ropes were donated for this purpose by the American Steel and Wire Co., and by the John A. Roebling's Sons Co. The ropes were of 6 by 19 construction, high-grade plow steel.

Ten specimens to be held by grips and ten specimens to have zinc sockets cast on the ends were cut alternately from the 130 foot length of each size of rope. The specimens to be tested in grips were 8 feet long, and those with sockets 5 feet long. The free length of each specimen (that is, the distance between the inner ends of the sockets or grips) was 4 feet. The specimens were numbered consecutively along the length of the ropes, those tested in grips having odd numbers and those with sockets, even numbers.

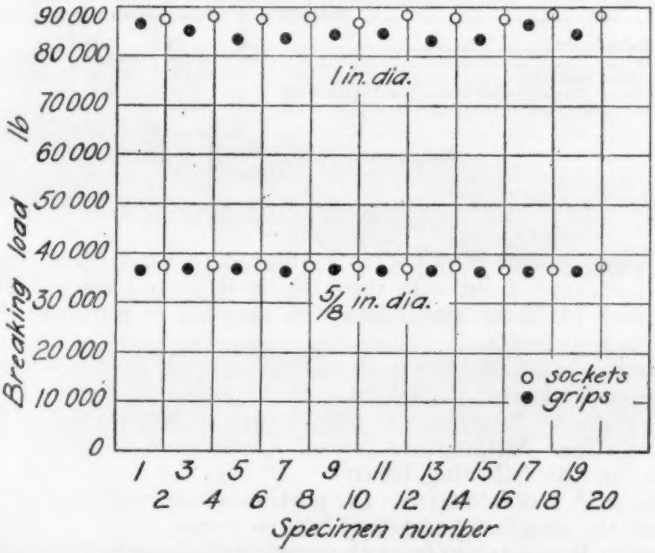

FIGURE 3.—*Tensile strength of new wire ropes held in grips and in sockets.*

The preparation of the specimens having sockets was carried out as described in Federal Specification RR–R–571 for wire rope, except that hot gasoline instead of muriatic acid was used for the final cleaning of the wires. The sockets were 6 inches long, 1⅞ inches in diameter at the small end of the cone, and 4⅛ inches in diameter at the large end.

All specimens of new wire rope were tested in a horizontal pendulum hydraulic machine having a capacity of 100,000 lb. This machine is shown in figure 1, and the grips are shown in figure 2. The grips were 19.25 inches long. They were lined with cast zinc and a 90-degree V-groove was machined in the zinc. The size of this groove depended upon the diameter of the rope to be tested. The compressive force on the grips caused by the tensile load on the rope during a test embedded the outside wires in the zinc. The same zinc linings were used for many tests of rope of the same size. The results of the tensile tests of these ropes are given in figure 3, and a summary of the results is given in table 1.

In order to expedite the work and reduce the cost, the committee approved the use of grips for the tensile tests of worn wire ropes having diameters not exceeding 1 inch because the differences between the results for grips and for sockets were negligible compared with the expected differences in the strengths of the worn ropes. Worn ropes having diameters exceeding 1 inch were socketed with zinc because the strength might exceed 100,000 lb, which is the capacity of the pendulum machine, and because the tests of new ropes indicated that the difference in percent between the results with grips and with sockets increased with size, being approximately proportional to the diameter.

TABLE 1.—*Summary of results of tensile tests of new wire ropes*

Wire rope diameter (in.)	⅝	⅝	1	1
Rope held in	Grips	Sockets	Grips	Sockets
Average breaking load (lb)	36,440	37,180	84,450	87,700
Average deviation of a single observation from the mean (%)	0.58	0.55	1.12	0.45
Difference in average breaking load (%)	−1.99		−3.53	

III. SPECIMENS

1. THE WORN WIRE ROPES

The users of wire ropes were requested to send three specimens, each 8 feet long, from wire rope removed from service. The rope represented by these specimens was assigned a number when the specimens were received.

Specimens from 79 ropes were submitted. Of these, 70 ropes were represented by 3 specimens, 1 rope by 6 specimens, 1 rope by 4 specimens, 2 ropes by 2 specimens, and 5 ropes by 1 specimen.

The specimen designations for each rope were assigned, as far as possible, on the following basis:

Specimen A was taken from the portion of the rope having the least wear and the smallest number of broken wires.

Specimen B was taken from the portion of the rope having average wear and an average number of broken wires.

Specimen C was taken from the portion of the rope having the greatest wear and the greatest number of broken wires.

A portion of each of these specimens from rope 20 is shown in figure 4.

Specimens A for 59 of the ropes had no visible broken wires or measurable wear. Either broken wires or wear or both were present on all the specimens from the other 20 ropes. The total number of specimens tested was 229.

2. CONSTRUCTION

The ropes represented 16 types of construction. For convenience, the types of construction have been given the numbers shown in table 2.

The number of worn wire ropes of each construction is given in table 3.

3. DATA FROM SERVICE-DATA SHEETS

The data from the service-data sheets which accompanied the specimens have been tabulated in table 4.

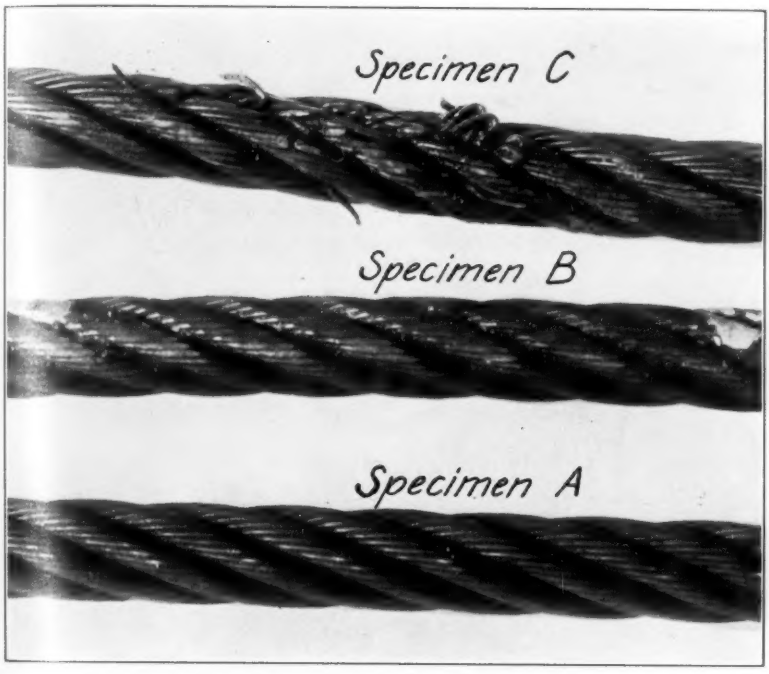

FIGURE 4.—*Specimens from rope 20.*

Specimen A.—Least wear and smallest number of broken wires.
Specimen B.—Average wear and average number of broken wires.
Specimen C.—Greatest wear and greatest number of broken wires.

TABLE 2.—*Wire-rope constructions*

Construction	See figure—	Number of strands and wires per strand	Trade name	Arrangement of wires						Type of core
				Center wires	Inside wires		Filler wires	Outside wires		
					S[1]	L[1]		S[1]	L[1]	
1	12, 18	6 by 7	Coarse laid rope	1					6	Fiber.
2	13, 19	6 by 19	Seale	1		9			9	Do.
3	15, 21	6 by 19	Roebling Special Seale	1		5	5		10	Do.
4	16, 22	6 by 19	Modified Seale	1		6	6		12	Do.
5	17	6 by 19	Warrington	1		6		6	6	Do.
6		6 by 37	Patented	1	9	9		9	9	Do.
7		8 by 19	Seale	1		9			9	Do.
8		8 by 19	Warrington	1		6		6	6	Do.
9		8 by 19	Modified Seale	1		6	6		12	Do.
10		7 by 7	Metallic center	1					6	7-wire strand.
11		6 by 19		1		6			12	Fiber.
12		6 by 37	(1+6+12+18). All wires in the outside layer had the same diameter. The next layer had large and small wires laid alternately. No filler wires. Fiber core.							
13		6 by 37	Construction 6, with independent wire-rope core of construction 5, regular lay.							
14		6 by 52	(1+6+9+18+18). All wires in the outside layer had the same diameter. The next layer had large and small wires laid alternately. No filler wires. Independent wire-rope core, construction 2, Lang lay.							
15		6 by 27	(1+6+10+10). All wires of each layer had the same diameter. No filler wires. Fiber core.							
16			Construction 3, with independent wire-rope core of construction 10.							
17		6 by 37	Construction 6, with independent wire-rope core of construction 2, regular lay.							
18	14, 20	6 by 16	Special Seale (1+4+8). Four filler wires. Fiber core.							

[1] S=Small wires, L=Large wires.

TABLE 3.—*Number of worn wire ropes of each construction*

Construction (see table 2)	Rope diameter, inches													
	¼	7/16	½	9/16	5/8	¾	1	1¼	1⅜	1½	1¾	1⅞	2¼	3¼
1							3							
2			4		48			3						
3			21					1	6		3			
4			3		9	3				3	6	3		
5		6	17	3	30			3						
6					6									
7			6											
8			3											
9									3					
11	3		6		3	3								
12						3								
13														7
14														3
15					2									
16											3			
17													3	

TABLE 4.—*Summary of service data sheets*

Rope	Nominal rope diameter	Construction	Lay	Material	Manufacturer[1]	Type of equipment	Loading	Service life		Mileage	Height of rise	Sheave diameter	Number of bends	Number of reverse bends
	in.						lb	*Years*	*Months*		ft	in.		
1	5/8	2	Regular	Traction steel	R	Elevator	[2] 6,000	7	2	53,340	250	36	3	0
2	1/2	5	do	Plow steel	R	Coal scraper	2,000	1	9	19,000		12	1	0
3	5/8	6	do	do	R	Crane	5,000	1	2		25	12	2	1
4	1/4	11	do			Hoist	500							
5	5/8	5	do	Traction steel	H	Pass. elevator	1,000	3	0	15,890	165	36 & 34	4	0
6	5/8	2	do	do	R	do		1	9	16,000	535	36	3	0
7	5/8	6	do	Plow steel		Crane	17,000	0	9		8+	18	2	2
8	5/8	2	do	Steel	R	Pass. elevator	3,000	7		74,000	250	32	2	0
9	3/4	12	do	High grade plow steel		Crane fall		5	5		30	18	1	3
10	1/2	7	do	Iron	M	Pass. elevator		4	4	20,000	270	17	2	0
11	1 1/4	2	Lang	Plow steel	R	Mine hoist	22,000			19,471	1,400	84	1	1
12	1 3/4	4	Lang left	Steel	R	do	36,726	0	6	16,255	1,086	144	2	0
13–1	1 3/4	3	Regular	Plow steel	A	Mine incline	38,000	0	7		1,269	144,	2	1
13–2	1 3/4	16	do	do	A	do	38,000	0	5		1,269	144	2	1
14	1/2	11	do	Iron	A	Freight elevator	3,000	4	0	1,659	75	30	1	0
15	3/4	4	do	do	A	Pass. elevator	1,500	3	3		93	36	1	0
16	1/2	7	do	Traction steel		do		3	1	700	39	22	2	0
17	1/2	5	do	Iron	R	do		6	4	14,000	113	16	2	0
18	9/16	5	do	Steel	M	do		1	1		120	30	5	2
19	5/8	5	do	do	R	do		8	5	289,308	120	48	4	0
20	5/8	11	do	Mild steel	R	do	2,000	3	9	2,728	45	28	3	1
21	5/8	2	do	Steel	R	Elevator	1,800	3	6	35,000	380	38	4	0
22	5/8	5	do	do		do	1,000	7	0	2,500	70	42	3	0
23	5/8	5	do	Iron	R	Pass. elevator	3,000	1	6			30	7	0
24	1 1/8	4	do	do	L	Mine hoist	56,000	1	7	11,321	700	120	2	0
25	7/16	5	do	do	R	Governor cable	100	2	2	14,093	308	18	4	0
26	1/2	8	do	do	R	Compensating cable	180	3	2	23,769	321	27	2	0
27	7/16	5	do	do	R	Governor cable	100	6	0	27,639	239	18	4	0
28	1/2	3	do	Traction steel	R	Pass. elevator		7	0		32	30	3	1
29	1 3/8	9	do	Improved plow	C							27	2	1
30	1 1/4	5	do	Steel	L	Slope hoist		2	0	14,000	563	48	2	0

31	1	1	Lang	do	R	do		2	10	30,000	393	36	6	0	
32	25/32	5	Regular	Mild steel	R	Pass. elevator	2,500	7	0	45,675	276	30	3	0	
33	1/2	2	do	Steel	R	do	1,200	3	0		125	24	1	0	
34	5/8	5	do	Iron	R	do	1,200	1	8		115	26	2	0	
35	1 5/16	3	Lang	Steel	R	Mine hoist	21,000	2	10			120	1	0	
36	1 5/16	3	do	do	R	do	21,000	2	10			120	1	0	
37	5/8	2	Regular	do	R	Pass. elevator	1,200	6	4	51,894	500	36	3	0	
38	5/8	2	do	Cast steel	R	Elevator	1,000	4	0			30	3	1	
39	5/8	2	do	Traction steel	R	Freight elevator	2,500	12	0	5,000	50	30	1	0	
40	5/8	2	do	Steel	R	Pass. elevator		2	6			34	1	0	
41	5/8	2	do	do	R	Freight elevator	[1] 8,000	4	7		15	30	1	0	
42	5/8	5	do	Iron		do	1,000	18	0	2,000	20	42	3	0	
43	1 1/2	4	Lang	Steel	A	Mine hoist	24,000	1	8		2,500	120	1	0	
44	9/16	2	Regular	Traction steel	C	Pass. elevator		5	9			36	2	0	
45	5/8	2	do	Steel		do	500	4	2		150	36	1	0	
46	5/8	2	do	do		do	500	4	2		150	36	1	0	
47	5/8	5	do	Traction steel		do	2,000	4	2		57	30	1	0	
48	5/8	4	do	Iron		do		3	0		91	36	1	0	
							yd/hr	working hr							
49	3 1/4	13	do	Plow steel	R	Dipper dredge (main hoist)	500	405–884			100	97	3	1	
50	3 1/4	14	do	do	A	do	500	311			100	97	3	1	
51	3 1/4	13	do	do	R	do	500	728			100	97	3	1	
52	2 1/4	17	do	do	C	do	500	291			100	97	3	1	
							lb	Years	Months						
53	1/2	2	do	Steel	R	Elevator	1,000				50	24	2	0	
54	1/2	3	do	do		Pass. elevator	500	1	6	1,400	85	24	4	3	
55	9/16	4	do	do	B	Freight elevator	1,000	11	8		45	26	3	0	
56	9/16	4	do	do	B	do	1,000	11	8		45	26	3	0	
57	9/16	5	do	do	A	Pass. elevator	1,200	5			60	30	2	0	
58	1/2	5	do	Iron	H	do	148	0	10	730	275	16	1	0	
59–1	1/2	3	do	Traction steel		do	2,500	2	6	11,668	75	26			
59–2	1/2	3	do	do		do	2,500	2	6	11,668	75	26			
59–3	1/2	3	do	do		do	2,500	2	6	11,668	75	26			
59–4	1/2	3	do	do		do	2,500	2	6	11,668	75	26			

See footnotes at end of table.

TABLE 4.—*Summary of service data sheets*—Continued

Rope	Nominal rope diameter	Construction	Lay	Material	Manufacturer[1]	Type of equipment	Loading	Service life		Mileage	Height of rise	Sheave diameter	Number of bends	Number of reverse bends
	in.						lb	*Years*	*Months*		ft	in.		
59–5	½	3	Regular	Traction steel		Pass. elevator	2,500	2	6	11,668	75	26		
60	½	5	do	Iron	C	Governor cable		2	8		(2)	16	2	0
61	½	5	do	do	C	do		2	8		(2)	16	2	0
62	5/16	5	do			Freight elevator	1,000				60	26	3	0
63	½	4	do	Steel	H	Pass. and freight	1,000	0	10	5,305	300	24	2	0
64	5/16	15	do	do	R	do	1,000	1	6		165	32	6	4
65	5/16	5	do	Iron		Pass. elevator	1,800	7	0		50	28	1	0
66	¾	11	do	do	R	do	500	13	7	8,000	50	48	2	0
67	½	11	do	Traction steel	R	Pass. and freight	1,500	6	10		25	24	3	0
68–1	½	5	do	Iron	R	Governor cable		3	0	13,990	260	16	2	0
68–2	½	5	do	do	R	do		4	11	27,408	260	16	2	0
69	5/16	2	do	Steel	R	Pass. elevator	1,000	4	5	46,217	300	32	2	0
70	5/16	2	do	do	R	do	1,000	4	5	44,359	380	32	2	0
71	5/16	2	do	do	R	do	1,000	2	5	39,359	380	32	2	0
72	1¼	3	Lang	High-grade plow steel	U	Mine hoist	8,000	2	0	415,624 metric ton kilometers	2,193	84	1	0

[1] A=American Steel and Wire Co.
B=Broderick and Bascom Rope Co.
C=American Cable Co.
H=Hazard Wire Rope Co.
L=A. Leschen and Sons Rope Co.
M=McWhyte Co.
R=John A. Roebling's Sons Co.
U=U. S. Steel Products Co.

[2] Total load on all ropes.

[3] 35 floors.

The rope specimens were supplied by the following firms:

Rope	Firm
1.	Engineering Societies Building, New York, N.Y.
2.	United States Aluminum Co., Edgewater, N. J.
3.	United Engineering and Foundry Co., Youngstown, Ohio.
4.	Shepard-Niles Crane and Hoist Corporation, Montour Falls, N. Y.
5.	Wall and Hanover Realty Co., New York, N. Y.
6.	40 Wall Street Bank, Manhattan, New York, N. Y.
7.	American Tube and Stamping Plant, Bridgeport, Conn.
8.	Travelers Insurance Co., Hartford, Conn.
9.	Navy Department, Washington, D. C.
10.	Zurich Insurance Co., Chicago, Ill.
11.	Phelps Dodge Corporation, Bisbee, Ariz.
12.	Miami Copper Co., Miami, Ariz.
13-1.	Clover Splint Coal Co., Pittsburgh, Pa.
13-2.	Clover Splint Coal Co., Pittsburgh, Pa.
14.	U. S. Casualty Co., Chicago, Ill.
15.	Hartford Accident and Indemnity Co., Hartford, Conn.
16.	Hartford Accident and Indemnity Co., Hartford, Conn.
17.	Globe Indemnity Co., New York, N.Y.
18.	Great American Indemnity Co., New York, N. Y.
19.	Hartford Accident and Indemnity Co., Hartford, Conn.
20.	U. S. Casualty Co., New York, N. Y.
21.	U. S. Casualty Co., New York, N. Y.
22.	U. S. Casualty Co., New York, N. Y.
23.	U. S. Casualty Co., New York, N. Y.
24.	Valier Coal Co., Valier, Ill.
25.	Ocean Accident and Guaranty Corporation, New York, N. Y.
26.	Ocean Accident and Guaranty Corporation New York, N. Y.
27.	Ocean Accident and Guaranty Corporation, New York, N. Y.
28.	The Travelers, Detroit, Mich.
29.	Utah Copper Co., Bingham, Utah.
30.	Union Pacific Coal Co., Rock Springs, Wyo.
31.	Union Pacific Coal Co., Rock Springs, Wyo.
32.	Standard Accident Insurance Co., Detroit, Mich.
33.	Travelers Insurance Co., Boston, Mass.
34.	Travelers Insurance Co., Boston, Mass.
35.	Corrigan McKinney Steel Co., Bessemer, Mich.
36.	Corrigan McKinney Steel Co., Bessemer, Mich.
37.	Equitable Building Corporation, New York, N. Y.
38.	Aetna Casualty and Surety Co., New York, N. Y.
39.	Aetna Life Insurance Co., New York, N. Y.
40.	Aetna Life Insurance Co., Hartford, Conn.
41.	Hartford Accident & Indemnity Co., Houston, Tex.
42.	Hartford Accident & Indemnity Co., Hartford, Conn.
43.	Montreal Mining Co., Hurley, Wis.
44.	National Association of Building Owners and Managers, Chicago, Ill.
45.	Aetna Life Insurance Co., Hartford, Conn.
46.	Aetna Life Insurance Co., Hartford, Conn.
47.	National Bureau of Standards, Washington, D. C.
48.	Aetna Life Insurance Co., Hartford, Conn.
49.	The Panama Canal, Dredging Division, Paraiso, Canal Zone.
50.	The Panama Canal, Dredging Division, Paraiso, Canal Zone.
51.	The Panama Canal, Dredging Division, Paraiso, Canal Zone.
52.	The Panama Canal, Dredging Division, Paraiso, Canal Zone.
53.	Hartford Accident and Indemnity Co., Manchester, N. H.
54.	Royal Indemnity Co., New York, N. Y.
55.	Aetna Life Insurance Co., Hartford, Conn.
56.	Aetna Life Insurance Co., Hartford, Conn.
57.	Continental Casualty Co., Chicago, Ill.
58.	Royal Indemnity Co., New York, N. Y.
59.	U. S. Department of Agriculture, Washington, D. C.
60.	Aetna Life Insurance Co., New York, N. Y.
61.	Aetna Life Insurance Co., New York, N. Y.
62.	Royal Indemnity Co., New York, N. Y.
63.	Aetna Life Insurance Co., New York, N. Y.
64.	Great American Indemnity Co., New York, N. Y.
65.	Hartford Accident and Indemnity Co., Philadelphia, Pa.
66.	Hartford Accident and Indemnity Insurance Co., Kansas City, Mo.
67.	Aetna Life Insurance Co., Hartford, Conn.
68.	Engineering Societies Building, New York, N. Y.
69.	Hartford Accident and Indemnity Insurance Co., Kansas City, Mo.
70.	Hartford Accident and Indemnity Insurance Co., Kansas City, Mo.
71.	Hartford Accident and Indemnity Insurance Co., Kansas City, Mo.
72.	El Potosi Mining Co., Chihuahua, Mexico.

The acceleration and deceleration of the load were given on the service-data sheets for only three ropes. It was not considered necessary to give these values.

IV. DESCRIPTION OF INSPECTION AND TESTS

1. TYPE OF LAY

The type of lay was determined by inspection. Ropes of regular right lay, Lang right lay, and Lang left lay were included in the investigation.

2. CONSTRUCTION

The construction of the rope was determined by unlaying the wires in a short length cut from specimen A, counting the number of wires in each layer, and observing whether they were of the same or of different diameters.

The designations for the construction were in accordance with table 2.

3. DIAMETER OF WIRES

The diameters of three wires in each layer, of three spacer wires (if any), and of the center wire were measured with a micrometer caliper to the nearest 0.001 inch. In the case of ropes of Warrington construction (nos. 5, 6, and 8) the diameters of two wires of each of the two sizes in the outside layer were measured. Average wire diameters were calculated to the nearest 0.0001 inch. These measurements were made on wires from specimen A.

4. DETERMINATION OF "WORST LAY"

The portion of a wire rope having the greatest number of broken wires and the greatest wear has the least tensile strength. The number of broken wires and the wear should be determined for a definite distance, as 1 foot or 1 rope lay. The rope lay is the distance, parallel to the axis of the rope, in which a strand makes one complete turn about the axis of the rope. One rope lay is probably better for this determination than a foot because a rope lay is proportional to the nominal diameter of the rope.

The location of the "worst lay" in these worn ropes was determined by inspection and not by an actual count of the number of broken wires in different rope lays. Usually there was little doubt as to which was the worst lay. For some specimens, however, one lay appeared to have about as many broken wires as another. As counting the broken wires in each lay for the entire length of the specimen did not appear to be justified, the observers used their best judgment in selecting the worst lay. Any difference there may have been between the lay selected as the worst lay and any lay having a greater number of broken wires is believed to be negligible. The worst lay was marked on the specimen by a paint mark at each end.

Some ropes had no broken wires and had, apparently, uniform wear. In such cases the midlength of the rope was considered the worst lay.

5. ROPE DIAMETER

The diameter of the rope was measured at three places along the worst lay to the nearest 0.001 inch. For ropes having a nominal diameter of not more than 1 inch a micrometer caliper was used and for ropes having a nominal diameter greater than 1 inch a vernier caliper was used. The three values were averaged for this report.

6. ROPE LAY

A length of five rope lays was marked on the specimen, the middle one being the worst lay. This length was measured to the nearest 0.1 inch. The rope lay was taken as one-fifth of this length and the values are given to the nearest 0.01 inch.

7. STRAND LAY

The number of wires in the outside layer of a strand had been counted to determine the rope construction. A length equal to five strand lays was measured to the nearest 0.05 inch. The strand lay was taken as one-fifth of this length and the values are given to the nearest 0.01 inch.

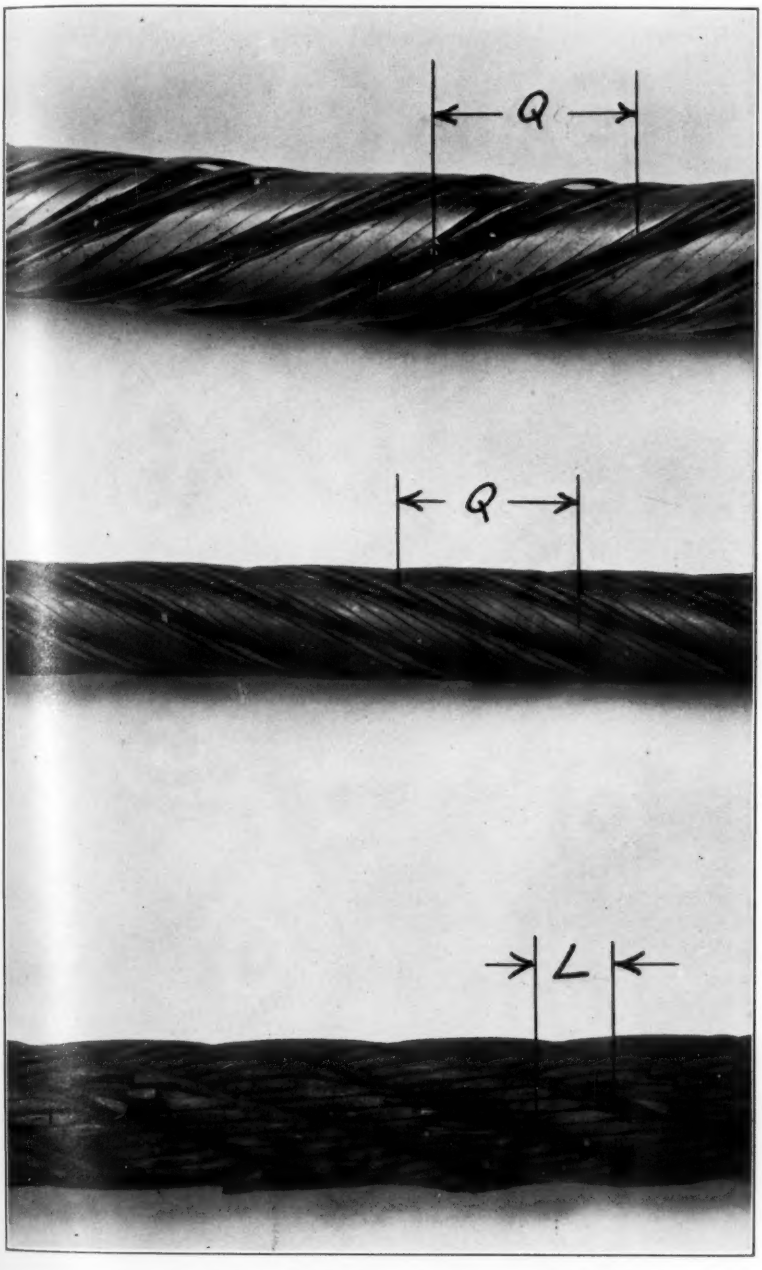

FIGURE 6.—*Wear on ropes of different types of lay.*

At top.—Rope 12–C, Lang lay rope, left lay.
Middle.—Rope 36–C, Lang lay rope, right lay.
Bottom.—Rope 13(1)–B, regular lay rope, right lay.
The distance Q on the Lang lay ropes and the distance L on the regular lay ropes is a measure of the wear.

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8. NUMBER OF BROKEN WIRES

The number and location of the broken wires in the worst lay of each specimen were determined for each strand. Both "crown breaks" on the crest of the strand and "valley breaks" were counted. A valley break is a break of a wire which is not on the surface of the rope but on the interior surface of a strand, where it faces and is in contact with another strand. The total number of broken wires in the rope, the number of strands having at least one broken wire, and the smallest number of strands for which the sum of the number of broken wires equaled or exceeded 80 percent of the total number of broken wires in the rope lay were determined.

9. WEAR

A worn outside wire of a regular lay wire rope is shown in figure 5. The smallest cross-sectional area, at X, hereafter referred to as the "remaining area", can be determined if d and either w or t is known. It is impossible to determine the value t by direct measurement unless the wire can be cut from the rope. The width of the worn surface w can be measured, but it is very small. Moreover, for each value of w (except when it is equal to d) there are two possible values of t, and hence the area is not uniquely determined from w and d. The length L of the worn surface, however, increases continuously as t decreases, and if a relation can be found between L and t for a given size of rope and type of construction, the remaining area can be found from the length L.

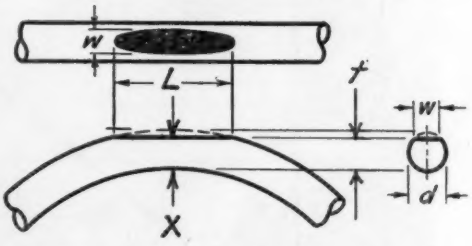

FIGURE 5.—*A worn outside wire of a regular lay rope.*

In this study, the length L was measured on five worn outside wires cut from the specimen after the tensile test had been made. It was found that the diameter of these wires was the same as the diameter before the test. If the length L was less than ¼ inch it was measured to the nearest 0.01 inch using a Brinell microscope having a scale in the field. If longer, it was measured using a steel scale.

On ropes of Warrington construction the length L was measured on three large and three small outside wires.

Lang lay ropes become worn in a slightly different manner, as may be seen in figure 6. While the length L is measurable on a Lang lay rope, the distance Q across a given number of wires is also a definite measure of the amount of wear and is more easily measured. For Lang lay rope, Q was measured between the closest points of wear on the first and fourth wires in a strand for ropes of 6 by 7 construction and between the closest points of wear on the first and sixth wires in a strand for ropes of 6 by 19 construction. It should be noted that as the wear increases, the distance Q becomes smaller. With no wear, Q is infinitely large.

10. REMAINING DIAMETER OF OUTSIDE WIRES

The length t, figure 5, which is the "remaining diameter" of the worn outside wires, was measured on the same wires on which the wear, L or Q, was determined. The measurements were made to the nearest 0.001 inch, using a micrometer caliper having either a ball or a line anvil.

11. REMAINING AREA OF THE ROPE

The area of the specimens was calculated by taking into account the number of wires not broken and the remaining diameter t of the

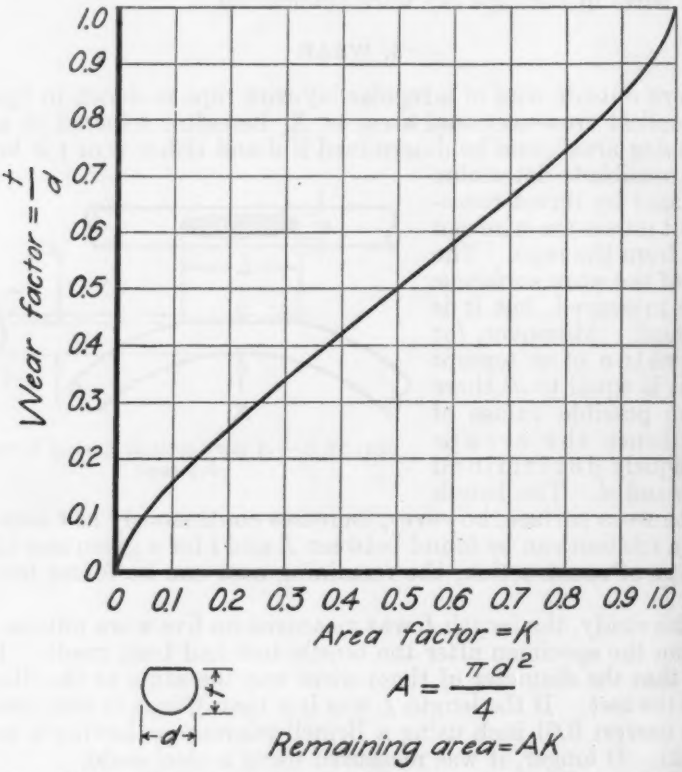

FIGURE 7.—*Relation between the remaining diameter of a worn wire and the cross-sectional area of the wire.*

outside wires. The cross-sectional area of a worn wire may be calculated by the aid of figure 7. In this figure, the ordinate represents the ratio of the remaining to the original diameter t/d, while corresponding values of area factors K are plotted as abscissas. If A is the cross-sectional area of the wire when no wear is present (diameter$=d$), then KA is the area of the worn wire for which the remaining diameter is t.

The areas of the inside wires were considered as full circles, and corresponding calculations were made.

In these calculations the total remaining area has been taken as the sum of the right sections across each separate wire. Actually in

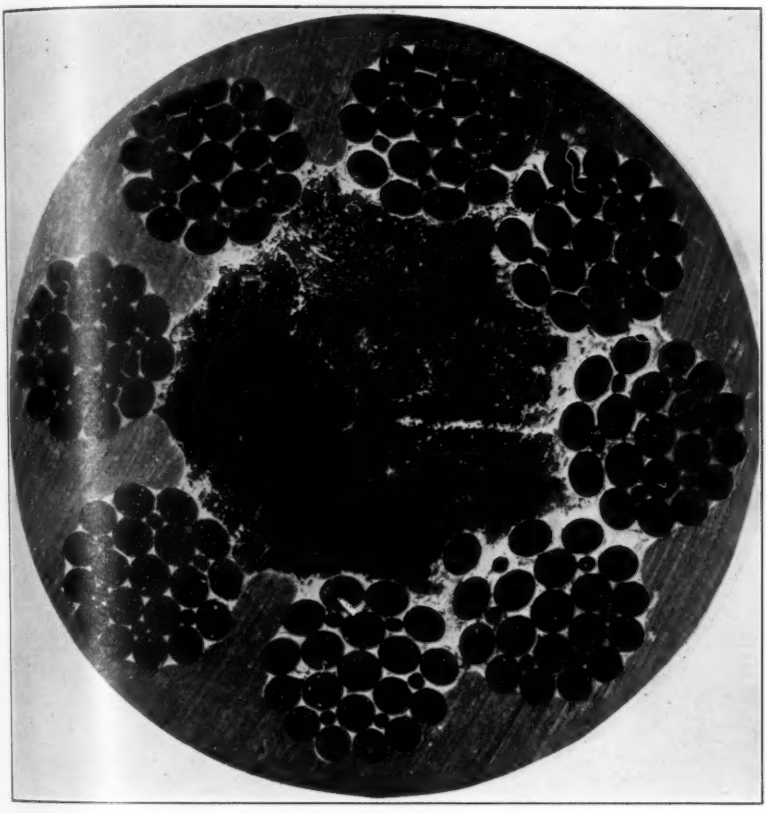

FIGURE 8.—*A section across rope* 29–C, *an 8-strand regular lay rope.*

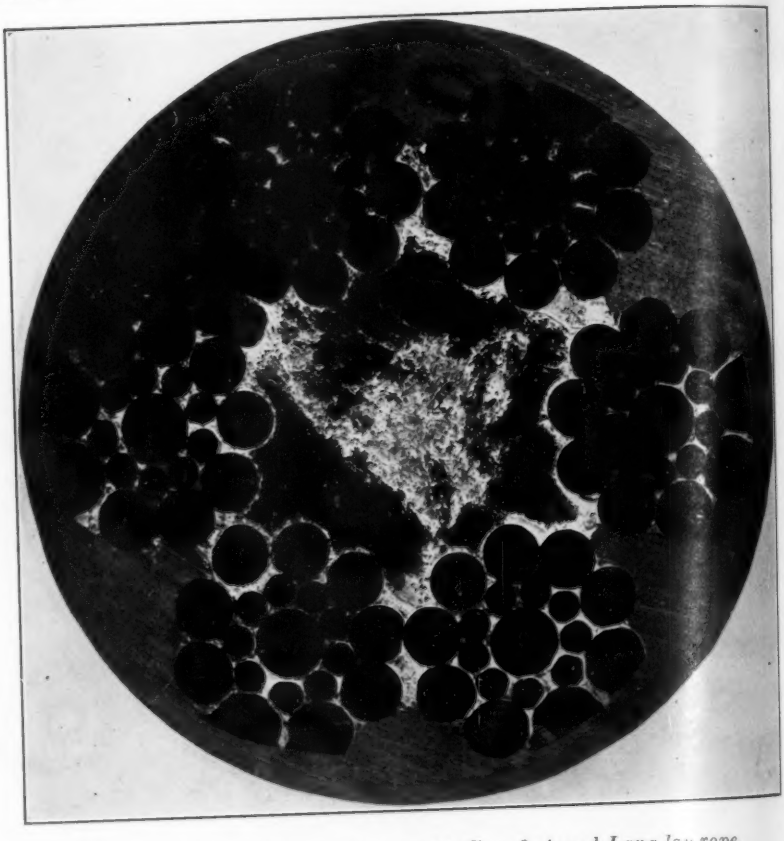

FIGURE 9.—*A section across rope* 11–C, *a 6-strand Lang lay rope.*

a rope, however, a right section across the rope does not cut all of the wires at right angles to their individual axes, as may be seen in figures 8 and 9. In the section of the regular lay rope, figure 8, the outside wires of each strand are cut very nearly at right angles to the axes of the wires, while the wires near the fiber core are cut at a relatively large angle to their axes. The reverse is obviously true in the section of the Lang lay rope, figure 9.

These figures show that in some cases the worn surface of the outside wires was deformed so that the sections are no longer portions of true circles. Generally, however, the area computed from the remaining diameter, t, is less than the actual remaining area and will therefore be on the side of safety if the tensile strength of the wire is not decreased by the wear.

12. CORE DIAMETER

The diameter of the fiber core near the end of each sample was measured to the nearest 0.01 inch, using a steel scale. This diameter was taken as the diameter of the inscribed circle of the cross section of the core.

13. CORE CONDITION

An estimation of the lubrication in the fiber core was made for each sample. It varied from "very dry" to "well lubricated". For the specimens having a "dry core" it was observed that no oil appeared on the surface of the rope during the tensile test, while in the specimens for which the core was considered well lubricated oil usually appeared on the surface of the rope at comparatively low tensile loads.

The fibers of the core were examined to determine whether or not they had been broken. For cores in apparently good condition the fibers were listed as long. In other cases short fibers were found in various proportions to the number of long fibers. The cores in a few ropes appeared to be rotted; the fibers were very short and appeared to have no tensile strength.

14. TENSILE TESTS

The specimens having a nominal diameter not greater than 1 inch were tested in a horizontal pendulum hydraulic testing machine, which could be adjusted for maximum loads of 10,000, 20,000, 50,000, and 100,000 lb. (see fig. 1). The ends of the specimen were held in grips 19.25 inches long. The free length was 4 feet for specimens having sufficient length. For the other specimens it was as long as the specimen permitted.

The specimens having a nominal diameter greater than 1 inch but less than 2¼ inches were tested in a vertical beam and poise testing machine having a capacity of 600,000 lb. but using an auxiliary poise which gave a maximum load of 300,000 lb. The specimens having a nominal diameter of 2¼ inches and 3¼ inches were tested in a horizontal fluid-support weighing scale testing machine having a capacity of 1,150,000 lb. in tension. The ends of the specimens were socketed with zinc. The free length was about 5 feet for these specimens.

The rate of separation of the heads of the testing machines was 0.4 in./min at no load.

The load at which oil appeared on the surface of the rope, the "breaking load" at which the rope failed, and the manner of failure were recorded.

The "tensile strength" was calculated by dividing the breaking load of the rope by the remaining area.

In this report the load at which the rope failed will be called the "breaking load" and the stress at failure the "tensile strength" (lb/in^2).

V. RESULTS OF INSPECTION AND TENSILE TESTS, WITH DISCUSSION

The results of the inspection and tensile tests of the ropes are given in table 5. Since, for many of these ropes, the wear and broken wires were distributed very uniformly along the length of the specimen, it is believed that the wear and broken-wire data given in table 5 adequately describe the ropes.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*

LAY REGULAR, RIGHT—CONSTRUCTION 2, 6 BY 19 SEALE

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires		Wear		Core		Rope			
						Strands [a]	Strands [b]	L	t/d	Diameter	Condition [c]	Breaking load	Remaining strength [d]	Remaining area	Tensile strength [e]
in.		in.	in.	in.				in.		in.		lb	%	in.^{2}	lb/in.^{2}
½	33–C	0.478	3.06	0.93	8	2	1	0.14	0.98	0.28	Ec	12,950	-----	0.0745	174,000
½	53–A	.488	3.16	.86	0	0	0	.00	1.00	.27	Aa	15,700	100	.0850	185,000
	–B	.470	3.22	.90	8	2	1	.12	.96	.27	Da	14,300	91	.0761	188,000
	–C	.466	3.22	.88	14	2	2	.11	.95	.26	Db	11,200	71	.0699	160,000
⅝	1(1)–A	.643	3.80	1.00	0	0	0	.00	1.00	.30	Aa	25,200	100	.1410	179,000
	–B	.616	3.88	1.02	0	0	0	.11	.97	.28	Dc	25,700	102	.1401	183,000
	–C	.618	3.84	1.06	0	0	0	.09	.99	.31	Dc	26,950	107	.1409	191,000
⅝	1(2)–A	.643	3.85	1.02	0	0	0	.00	1.00	.32	Aa	25,450	100	.1435	177,000
	–B	.621	3.94	1.03	0	0	0	.12	.94	.31	Dd	25,740	101	.1409	183,000
	–C	.624	3.86	1.04	0	0	0	.13	.92	.33	Dd	25,950	102	.1399	186,000
⅝	6–A	.627	4.04	1.08	0	0	0	.19	.95	.26	Aa	25,450	98	.1419	180,000
	–B	.603	4.02	1.07	3	1	1	.15	.93	.28	Da	25,000	97	.1359	184,000
	–C	.595	4.14	1.09	5	2	1	.13	.94	.30	Db	23,200	90	.1327	175,000
⅝	8–A	.633	3.86	1.10	0	0	0	.00	1.00	.30	Aa	25,300	100	.1449	175,000
	–B	.607	3.88	1.04	2	1	1	.16	.92	.30	Dc	22,950	91	.1377	166,000
	–C	.584	3.98	.99	14	4	3	.15	.91	.30	Dc	19,850	78	.1165	170,000
⅝	21–A	.617	3.82	1.02	0	0	0	.00	1.00	.28	Ba	25,200	100	.1403	180,000
	–B	.594	3.83	1.02	0	0	0	.12	.94	.29	Dc	25,000	99	.1381	181,000
	–C	.598	3.84	1.05	12	3	2	.15	.93	.29	Db	23,600	94	.1172	201,000
⅝	37–A	.630	3.80	1.01	0	0	0	.00	1.00	.30	Aa	25,100	100	.1462	172,000
	–B	.615	3.90	1.05	5	1	1	.16	.94	.30	Dc	24,700	98	.1346	184,000
	–C	.617	3.95	1.04	11	3	2	.15	.93	.28	Dc	17,850	71	.1234	145,000
⅝	38–A	.620	3.76	1.03	0	0	0	.00	1.00	.30	Aa	25,820	100	.1497	172,000
	–B	.620	3.86	1.06	8	2	2	.11	.96	.31	Da	17,800	69	.1336	133,000
	–C	.609	3.84	1.05	21	3	2	.14	.95	.30	Ca	17,100	66	.1090	157,000
⅝	39–A	.619	3.82	1.00	0	0	0	.00	1.00	.29	Aa	25,250	100	.1444	175,000
	–B	.617	3.87	1.03	9	5	4	.14	.94	.31	Cc	22,450	89	.1258	178,000
	–C	.606	3.86	1.03	12	6	4	.14	.93	.30	Cb	22,200	88	.1202	185,000

See footnotes at end of table.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*—Continued

LAY REGULAR, RIGHT—CONSTRUCTION 2, 6 BY 19 SEALE—Continued

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires		Wear		Core		Rope			
						Strands [a]	Strands [b]	L	t/d	Diameter	Condition [c]	Breaking load	Remaining strength [d]	Remaining area	Tensile strength
in.		in.	in.	in.				in.		in.		lb	%	in.²	lb/in.²
5/8	40-A	.642	3.86	1.04	0	0	0	.00	1.00	.30	Aa	25,150	100	.1458	172,000
	-B	.617	3.87	1.04	8	3	2	.11	.97	.30	Ca	20,600	82	.1304	158,000
	-C	.626	3.93	1.01	14	3	2	.11	.96	.31	Ac	19,300	77	.1194	162,000
5/8	41-A	.620	3.88	1.02	0	0	0	.00	1.00	.30	Ac	25,550	100	.1447	176,000
	-B	.600	3.97	1.05	29	6	4	.13	.96	.29	Dc	17,500	69	.0914	192,000
	-C	.593	4.01	1.04	37	6	5	.13	.96	.30	Dc	15,250	60	.0772	198,000
5/8	44-A	.633	3.75	1.04	0	0	0	.00	1.00	.30	Aa	22,800	100	.1440	158,000
	-B	.620	3.85	1.01	6	4	3	.10	.97	.33	Dc	20,050	88	.1321	152,000
	-C	.614	3.88	1.04	7	3	3	.08	.98	.33	Dc	17,750	78	.1306	136,000
5/8	45-A	.631	3.81	1.05	0	0	0	.00	1.00	.32	Aa	25,150	100	.1449	174,000
	-B	.616	3.88	1.03	2	1	1	.15	.92	.28	Db	24,750	98	.1376	180,000
	-C	.608	3.86	1.02	5	1	1	.15	.94	.27	Dc	22,950	91	.1334	172,000
5/8	46-A	.624	3.80	1.00	0	0	0	.00	1.00	.24	Aa	25,200	100	.1463	172,000
	-B	.626	3.84	1.03	0	0	0	.13	.99	.31	Ca	25,450	101	.1462	174,000
	-C	.613	3.92	1.02	5	1	1	.13	.96	.31	Cd	22,000	87	.1357	162,000
5/8	69-A	.624	3.92	1.04	0	0	0	.00	1.00	.31	Aa	23,800	100	.1445	165,000
	-B	.596	3.96	1.20	12	3	2	.11	.98	.31	Dc	18,800	79	.1225	153,000
	-C	.603	3.96	1.20	22	6	3	.11	.96	.31	Cb	11,500	48	.1038	111,000
5/8	70-A	.619	3.93	1.04	0	0	0	.00	1.00	.31	Ba	25,000	100	.1445	173,000
	-B	.596	3.90	1.04	0	0	0	.09	.96	.32	Cb	25,400	102	.1431	177,000
	-C	.608	4.00	1.03	19	6	4	.10	.96	.32	Ba	19,700	79	.1092	180,000
5/8	71-A	.649	3.88	1.04	0	0	0	.00	1.00	.32	Aa	24,000	100	.1399	172,000
	-B	.622	3.92	1.05	0	0	0	.10	.99	.35	Bc	25,400	106	.1398	181,000
	-C	.629	3.99	1.04	14	5	3	.10	.95	.37	Dc	15,800	66	.1141	138,000

LAY REGULAR, RIGHT—CONSTRUCTION 3, 6 BY 19, ROEBLING SPECIAL SEALE

1/2	28-A	0.497	3.11	0.89	0	0	0	0.00	1.00	0.27	Aa	16,350	100	0.0890	184,000
	-B	.481	3.15	.87	5	2	1	.10	.94	.24	Cb	17,200	105	.0832	207,000
	-C	.473	3.18	.84	13	2	2	.13	.91	.23	Cc	13,200	81	.0753	175,000
1/2	54-A	.495	3.18	.92	0	0	0	.00	1.00	.28	Aa	16,800	100	.0903	186,000
	-B	.496	3.19	.89	0	0	0	.08	.96	.28	Db	16,800	100	.0896	188,000
	-C	.481	3.26	.91	20	5	2	.09	.96	.25	Dc	11,600	69	.0713	163,000
1/2	59-1-A	.487	3.00	.82	0	0	0	.00	1.00	.30	Ca	17,200	100	.0893	193,000
	-B	.495	2.99	.87	0	0	0	.00	1.00	.26	Ca	16,800	98	.0893	188,000
	-C	.490	3.01	.86	2	2	2	.10	.96	.25	Da	17,000	99	.0852	199,000
1/2	59-2-A	.497	3.01	.86	0	0	0	.00	1.00	.29	Ca	16,800	100	.0890	189,000
	-B	.484	3.00	.85	6	3	2	.11	.97	.25	Cb	16,500	98	.0832	198,000
	-C	.485	3.01	.86	9	2	2	.11	.91	.24	Cb	15,600	93	.0789	198,000
1/2	59-3-A	.491	3.01	.87	0	0	0	.00	1.00	.26	Ca	17,200	100	.0893	193,000
	-B	.487	3.01	.87	1	1	1	.00	1.00	.26	Ca	17,000	99	.0884	192,000
	-C	.475	2.95	.87	6	1	1	.11	.94	.25	Cb	15,700	91	.0826	190,000
1/2	59-4-A	.509	2.92	.85	0	0	0	.00	1.00	.23	Ca	16,600	100	.0890	186,000
	-B	.492	2.96	.88	2	1	1	.10	.94	.24	Ca	16,400	99	.0860	191,000
	-C	.483	3.08	.90	4	1	1	.09	.97	.22	Cb	16,800	101	.0850	198,000
1/2	59-5-A	.499	2.92	.84	0	0	0	.00	1.00	.26	Ca	16,600	100	.0863	192,000
	-B	.491	2.98	.83	2	1	1	.10	.97	.26	Ca	17,700	107	.0842	210,000
	-C	.497	2.97	.87	4	2	2	.00	1.00	.27	Cb	16,500	99	.0829	199,000
1 1/4	13(1)-A	1.814	10.20	2.88	0	0	0	.29	.99	1.00	Ca	245,800	100	1.249	196,000
	-B	1.680	11.48	2.86	26	6	3	.75	.85	.78	Dc	171,500	70	.863	199,000
	-C	1.691	11.46	2.86	40	6	4	.75	.85	.78	Dc	158,100	64	.694	228,000

See footnotes at end of table.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*—Continued

LAY REGULAR, RIGHT—CONSTRUCTION 4, 6 BY 19, MODIFIED SEALE

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires		Wear		Core		Rope			
						Strands [a]	Strands [b]	L	t/d	Diameter	Condition [c]	Breaking load	Remaining strength [d]	Remaining area	Tensile strength
in.		in.	in.	in.				in.		in.		lb	%	in.²	lb/in.²
½	63-A	0.514	3.12	0.85	0	0	0	0.00	1.00	0.28	Da	15,800	100	0.0990	160,000
	-B	.503	3.15	.85	2	2	2	.09	.97	.26	Ca	16,200	103	.0968	167,000
	-C	.509	3.09	.85	6	3	2	.08	.97	.27	Cb	16,700	106	.0936	178,000
9/16	48-A	.616	3.80	1.05	0	0	0	.00	1.00	.28	Aa	12,750	100	.1498	85,000
	-B	.612	3.86	1.04	3	3	3	.10	.95	.27	Db	12,500	98	.1446	86,000
	-C	.607	3.84	1.04	3	1	1	.13	.93	.27	Da	12,500	98	.1437	87,000
5/8	55-A	.654	4.64	1.24	0	0	0	.00	1.00	.28	Aa	37,250	100	.1605	232,000
	-B	.640	4.60	1.25	3	2	2	.00	1.00	.28	Aa	36,500	98	.1565	233,000
	-C	.613	4.68	1.26	9	4	3	.11	.99	.29	Aa	35,250	95	.1483	238,000
5/8	56-A	.638	4.60	1.24	0	0	0	.00	1.00	.26	Aa	37,050	100	.1658	223,000
	-B	.648	4.58	1.24	1	1	1	.00	1.00	.29	Aa	37,000	100	.1645	225,000
	-C	.628	4.62	1.29	21	6	5	.00	1.00	.29	Da	33,650	91	.1367	246,000
¾	15-A	.750	4.74	1.34	0	0	0	.14	.95	.34	Aa	18,700	99	.2201	85,000
	-B	.746	4.80	1.32	0	0	0	.20	.89	.37	Aa	18,150	96	.2154	84,000
	-C	.737	4.80	1.30	35	6	5	.20	.88	.32	Ca	16,600	88	.1580	105,000
1 7/8	24-A	1.779	13.90	3.70	0	0	0	.00	1.00	.80	Aa	260,900	100	1.323	197,000
	-B	1.745	13.90	3.68	0	0	0	.45	.98	.83	Ca	259,400	100	1.319	197,000
	-C	1.732	14.10	3.64	5	5	5	.38	.95	.82	Da	253,500	97	1.255	202,000

LAY REGULAR, RIGHT—CONSTRUCTION 5, 6 BY 19, WARRINGTON

7/16	25-A	0.439	2.80	0.75	0	0	0	0.00	1.00	0.17	Aa	5,600	100	0.0773	72,000
	-B	.448	2.79	.75	0	0	0	.09	.92	.16	Ca	5,650	101	.0761	74,000
	-C	.440	2.82	.76	111	6	6	.08	.92	.19	Da	360	6	.0024	------
7/16	27-A	.499	3.01	.92	0	0	0	.00	1.00	.18	Da	8,400	100	.1000	84,000
	-B	.488	3.06	.94	0	0	0	.08	.99	.21	Da	8,400	100	.0998	84,000
	-C	.509	3.12	.90	f 45	6	4	.10	.97	.17	Da	1,700	20	.0625	27,000
½	2-A	.466	3.10	.88	0	0	0	.21	.57	.20	Ca	11,350	78	.0797	142,000
	-B	.475	2.89	.91	0	0	0	.26	.58	.21	Da	10,950	76	.0801	137,000
	-C	.449	3.14	.88	14	6	5	.28	.60	.20	Dd	9,850	68	.0736	134,000
½	17-A	.508	2.98	.87	0	0	0	.00	1.00	.24	Aa	11,500	100	.1048	110,000
	-B	.503	3.08	.85	6	2	2	.10	.93	.23	Cb	9,300	81	.0981	95,000
	-C	.508	3.04	.87	45	5	4	.09	.95	.21	Ca	7,400	64	.0657	113,000
½	58-A	.507	3.20	.88	0	0	0	.00	1.00	.27	Ba	11,200	100	.0947	118,000
	-B	.503	3.24	.85	0	0	0	.00	1.00	.22	Ca	9,700	87	.0947	102,000
	-C	.507	3.27	.86	g 14	1	1	.12	.94	.21	Ca	1,900	17	.0629	23,000
½	60-C	.452	2.82	.75	h 19	1	1	.10	.93	.20	Ca	2,400	-----	.0650	36,200
½	61-A	.456	2.80	.71	0	0	0	.00	1.00	.21	Ca	5,700	100	.0835	68,000
½	68-1-A	.504	3.20	.89	2	2	2	.07	.96	.24	Ba	10,000	98	.0992	101,000
	-B	.506	3.14	.96	7	3	2	.08	.95	.22	Ca	9,800	96	.0946	103,000
	-C	.505	3.17	.84	10	4	3	.05	.98	.22	Ca	10,300	101	.0932	111,000
½	68-2-A	.508	3.09	.89	0	0	0	.00	1.00	.22	Ca	12,200	100	.1040	117,000
	-B	.496	3.14	.88	6	2	1	.12	.87	.22	Ca	9,500	78	.0951	100,000
	-C	.493	3.20	.90	30	5	3	.12	.87	.22	Ca	8,200	67	.0762	108,000
9/16	18-A	.569	3.46	1.07	0	0	0	.00	1.00	.27	Db	23,550	100	.1326	178,000
	-B	.571	3.45	1.05	0	0	0	.00	1.00	.25	Aa	22,900	97	.1326	172,000
	-C	.565	3.50	1.12	9	5	4	.10	.97	.25	Ca	20,250	86	.1219	166,000
5/8	5-A	.623	3.82	1.08	0	0	0	.08	.96	.28	Da	19,750	99	.1635	121,000
	-B	.609	3.79	1.10	7	5	4	.12	.96	.28	Da	19,650	99	.1529	128,000
	-C	.602	3.84	1.09	14	6	5	.10	.95	.28	Da	19,600	98	.1446	136,000

See footnotes at end of table.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*—Continued

LAY REGULAR, RIGHT—CONSTRUCTION 5, 6 BY 19 WARRINGTON—Continued

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires: Strands [a]	Strands [b]	Wear: L	Wear: t/d	Core: Diameter	Core: Condition [c]	Rope: Breaking load	Rope: Remaining strength [d]	Rope: Remaining area	Rope: Tensile strength
in.		in.	in.	in.				in.		in.		lb	%	in.²	lb/in.²
	19-A	0.624	3.70	1.02	0	0	0	0.00	1.00	0.30	Aa	18,300	100	0.1505	122,000
5/8	-B	.605	3.68	1.05	18	4	2	.12	.92	.28	Bc	17,500	96	.1269	138,000
	-C	.615	3.74	1.05	28	5	3	.13	.92	.29	Cc	16,700	91	.1155	145,000
	22-A	.590	3.74	1.14	0	0	0	.00	1.00	.28	Ca	10,850	100	.1466	74,000
5/8	-B	.572	3.77	1.15	1	1	1	.30	.66	.28	Da	10,050	93	.1193	84,000
	-C	.557	3.77	1.10	4	2	2	.24	.76	.27	Da	9,958	92	.1268	78,000
	23-A	.615	3.78	1.04	0	0	0	.00	1.00	.28	Aa	17,000	100	.1503	113,000
5/8	-B	.598	3.84	1.08	0	0	0	.20	.76	.28	Ab	14,350	84	.1331	108,000
	-C	.594	3.92	1.06	22	6	4	.18	.86	.28	Ac	13,300	78	.1190	112,000
	32-A	.649	3.54	1.16	0	0	0	.00	1.00	.30	Aa	20,300	100	.1592	128,000
5/8	-B	.612	3.65	1.18	5	3	2	.24	.84	.28	Dc	18,800	93	.1389	135,000
	-C	.608	3.68	1.16	10	4	3	.14	.95	.28	Ed	19,300	95	.1440	134,000
5/8	34-C	.602	3.80	1.00	19	5	4	.12	.89	.32	Aa	14,200	-----	.1212	117,000
	42-A	.660	4.10	1.14	0	0	0	.00	1.00	.27	Aa	28,750	100	.1740	165,000
5/8	-B	.651	4.26	1.18	0	0	0	.00	1.00	.30	Aa	28,800	100	.1740	166,000
	-C	.633	4.16	1.18	0	0	0	.28	.73	.28	Aa	25,100	87	.1515	166,000
	47-A	.643	3.82	1.08	0	0	0	.00	1.00	.28	Da	19,650	100	.1685	117,000
5/8	-B	.610	3.84	1.12	8	4	3	.10	.96	.28	Db	19,650	100	.1562	126,000
	-C	.606	3.92	1.12	19	6	4	.14	.93	.27	Db	19,200	98	.1399	137,000
	57-A	.516	3.38	.93	0	0	0	.00	1.00	.30	Ca	21,500	100	.1064	202,000
5/8	-B	.492	3.40	.95	3	2	2	.19	.75	.24	Ca	21,300	99	.0908	235,000
	-C	.491	3.40	.89	4	1	1	.19	.74	.28	Ca	20,200	94	.0924	219,000
	62-A	.654	3.84	1.11	0	0	0	.00	1.00	.30	Aa	20,700	100	.1590	130,000
5/8	-B	.633	3.89	1.12	3½	3	3	.18	.85	.31	Aa	11,600	56	.1469	79,000
	-C	.645	3.68	1.20	55	6	5	.16	.92	.31	Ab	7,100	34	.0871	82,000
	65-B	.612	3.86	1.06	28	6	4	.16	.87	.31	Ba	8,000	-----	.1187	67,000
5/8	-C	.600	3.85	1.09	44	5	3	.18	.83	.31	Ca	6,600	-----	.0950	69,000
	30-A	1.23	9.62	2.44	0	0	0	.61	.82	.52	Ca	124,850	93	.6196	202,000
1¼	-B	1.16	9.20	2.50	3	2	2	.70	.60	.48	Db	109,500	81	.5143	213,000
	-C	1.16	9.34	2.48	22	5	2	.74	.64	.50	Db	85,800	64	.4619	186,000

LAY REGULAR, RIGHT—CONSTRUCTION 6, 6 BY 37, PATENTED

	3-A	0.672	3.80	1.09	0	0	0	0.00	1.00	0.33	Da	34,950	100	0.1700	205,000
3/4	-B	.645	3.88	1.11	12	4	3	.16	.87	.31	Dc	34,800	100	.1569	222,000
	-C	.667	3.76	1.14	50	4	2	.00	1.00	.32	Da	16,000	46	.1313	122,000
	7-A	.685	3.94	1.15	0	0	0	.00	1.00	.32	Aa	33,650	100	.1584	212,000
3/4	-B	.621	4.00	1.18	4	3	3	.28	.88	.28	De	32,650	97	.1516	215,000
	-C	.605	4.06	1.22	101	6	6	-----	-----	.29	De	24,200	72	.0954	254,000

LAY REGULAR, RIGHT—CONSTRUCTION 7, 8 BY 19 SEALE

	10-A	0.488	3.16	0.82	0	0	0	0.16	0.82	0.28	Da	4,500	92	0.0758	59,000
½	-B	.486	3.22	.79	34	7	5	.16	.79	.28	Ca	3,100	63	.0517	60,000
	-C	.475	3.08	.84	50	8	6	.14	.86	.27	Cb	2,550	52	.0424	60,000
	16-A	.498	3.17	.78	0	0	0	.00	1.00	.27	Aa	11,550	100	.0848	136,000
½	-B	.496	3.16	.78	10	6	4	.09	.95	.26	Dc	10,860	94	.0759	143,000
	-C	.481	3.24	.79	30	7	3	.08	.97	.27	Dc	9,650	83	.0603	160,000

See footnotes at end of table.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*—Continued

LAY REGULAR, RIGHT—CONSTRUCTION 8, 8 BY 19 WARRINGTON

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires		Wear		Core		Rope			
						Strands [a]	Strands [b]	L	t/d	Diameter	Condition [c]	Breaking load	Remaining strength [d]	Remaining area	Tensile strength
in.		in.	in.	in.				in.		in.		lb.	%	in.²	lb/in.²
½	26–A	0.511	2.82	0.73	0	0	0	0.00	1.00	0.30	Aa	5,950	100	0.0798	74,000
	–B	.515	2.88	.72	0	0	0	.16	.87	.30	Ca	4,550	76	.0748	61,000
	–C	.489	2.91	.79	16	3	2	.17	.66	.26	Da	3,950	66	.0576	69,000

LAY REGULAR, RIGHT—CONSTRUCTION 9, 8 BY 19 MODIFIED SEALE

1⅜	29–A	1.380	8.22	1.84	0	0	0	0.00	1.00	0.80	Ca	127,800	100	0.6218	206,000
	–B	1.320	8.10	1.86	0	0	0	.37	.79	.70	Ca	121,900	95	.5684	214,000
	–C	------	------	------	[1] 95	5	5	.51	.73	.70	Ca	22,350	17	.2048	109,000

LAY REGULAR, RIGHT—CONSTRUCTION 11

¼	4–A	0.267	1.49	0.55	3	3	3	0.11	0.94	0.16	Ba	4,600	96	0.0250	184,000
	–B	.271	1.50	.51	7	6	5	.14	.88	.12	Ba	4,750	99	.0235	202,000
	–C	.255	1.57	.58	10	6	4	.12	.88	.12	Bb	4,200	88	.0228	184,000
½	14–A	.507	3.04	.92	0	0	0	.00	1.00	.20	Aa	6,650	100	.1009	66,000
	–B	.501	3.08	.94	10	3	2	.18	.87	.20	Ca	6,200	93	.0873	71,000
	–C	.490	3.10	.91	38	6	5	.18	.86	.22	Ea	5,100	77	.0631	81,000
½	67–A	.487	3.23	1.06	0	0	0	.00	1.00	.21	Aa	7,000	100	.0870	80,000
	–B	.466	3.40	1.11	60	6	5	.12	.84	.22	Da	5,200	74	.0407	128,000
	–C	.464	3.40	1.11	60	6	5	.14	.90	.22	Eb	4,600	66	.0412	111,000
⅝	20–A	.614	3.55	1.08	0	0	0	.16	.91	.26	Cc	8,800	97	.1476	60,000
	–B	.598	3.66	1.10	7	4	3	.34	.57	.29	Db	7,450	82	.1075	69,000
	–C	.594	3.60	1.11	28	4	3	.34	.59	.29	Da	6,650	73	.0923	72,000
¾	66–A	.749	4.64	1.29	0	0	0	[m].00	1.00	.36	Aa	13,700	100	.2087	66,000
	–B	.720	4.71	1.30	0	0	0	.23	.87	.35	Ca	14,700	107	.1992	74,000
	–C	.725	4.71	1.36	15	2	2	.25	.83	.35	Ca	8,000	58	.1704	47,000

LAY REGULAR, RIGHT—CONSTRUCTION 12

¾	9–A	0.751	4.90	1.60	1	1	1	0.33	0.73	0.30	Da	39,360	90	0.2122	185,000
	–B	.728	4.72	1.59	1	1	1	.33	.71	.32	De	36,450	84	.2087	175,000
	–C	.730	5.50	1.54	15	4	2	.36	.66	.30	De	34,920	80	.1936	180,000

LAY REGULAR, RIGHT—CONSTRUCTION 13

3¼	49–A	------	------	------	0	0	0	0.00	1.00	-----	Aa	985,000	100	5.029	196,000
	–B (2)	3.16	20.9	6.0	6	3	2	.63	.93	0.50	Dc	901,000	91	4.824	187,000
	–B (1)	3.21	21.4	6.4	73	6	5	1.16	.74	.48	Dc	700,000	71	3.489	201,000
	–C (3)	3.18	20.8	6.4	[n] 127	6	6	.69	.92	.49	Dc	429,000	44	2.563	167,000
3¼	51–A	3.35	------	------	0	0	0	.00	1.00	-----	Aa	957,000	100	5.028	190,000
	°–B (6)	3.18	21.6	6.8	4	3	3	.77	.90	.69	Dd	899,000	94	4.874	184,000
	°–C (7)	3.17	21.7	6.8	95	6	6	.71	.87	.73	Dd	727,000	76	3.180	229,000

LAY REGULAR, RIGHT—CONSTRUCTION 14

3¼	50–A	------	------	------	0	0	0	0.00	1.00	-----	Aa	918,000	100	4.984	184,000
	–B (4)	3.23	20.9	6.4	0	0	0	1.30	.74	.72	Dd	903,000	99	4.611	197,000
	[p] –C (5)	3.33	20.0	6.2	[q] 10	----	----	.00	1.00	.70	Dd	825,000	90	4.887	169,000

See footnotes at end of table.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*—Continued

LAY REGULAR, RIGHT—CONSTRUCTION 15

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires		Wear		Core		Rope			
						Strands [a]	Strands [b]	L	t/d	Diameter	Condition [c]	Breaking load	Remaining strength [d]	Remaining area	Tensile strength
in.		in.	in.	in.				in.		in.		lb.	%	in.²	lb/in.
⅝	64-A	0.617	3.90	1.05	0	0	0	0.00	1.00	.32	Ba	24,100	100	0.1395	173,000
	-C	.593	3.99	1.05	18	4	3	.21	.74	.32	Aa	14,200	59	.1009	141,000

LAY REGULAR, RIGHT—CONSTRUCTION 16

1¼	13(2)-A	1.793	11.00	2.90	0	0	0	.51	0.99	-----	-----	282,200	100	1.483	190,000
	-B	1.709	11.55	2.98	30	6	4	.72	.99	-----	-----	199,300	71	1.086	183,000
	-C	1.719	11.28	2.98	58	6	6	.76	.85	-----	-----	164,500	58	.714	230,000

LAY REGULAR, RIGHT—CONSTRUCTION 17

2¼	52-A	2.30	-------	------	0	0	0	0.00	1.00	-----	Aa	397,000	100	2.2876	174,000
	-B(9)	2.23	14.1	4.4	4	2	2	.00	1.00	.40	Cb	360,000	91	2.2548	160,000
	-C(8)	2.23	14.3	5.1	54	6	5	.00	1.00	.40	Cc	297,000	75	1.8546	160,000

LAY, LANG, RIGHT—CONSTRUCTION 1, 6 BY 7 COARSE LAID

								Wear							
								Q	t/d						
								in.							
1	31-A	0.949	7.92	5.48	0	0	0	2.40	0.84	0.48	Dc	70,000	92	0.3662	191,000
	-B	.948	8.08	5.42	0	0	0	2.22	.84	.53	Dc	75,000	98	.3662	205,000
	-C	.911	8.20	6.14	2	2	2	2.37	.82	.48	Dc	44,000	58	.3434	128,000

LAY, LANG, RIGHT—CONSTRUCTION 2, 6 BY 19 SEALE

1¼	11-A	1.307	8.66	5.10	0	0	0	2.50	0.89	0.70	Ca	137,500	96	0.6258	220,000
	-B	1.207	8.85	5.20	1	1	1	2.09	.78	.67	Da	128,500	90	.5685	226,000
	-C	1.173	8.84	5.31	1	1	1	2.10	.76	.60	Da	122,700	86	.5595	220,000

LAY, LANG, RIGHT—CONSTRUCTION 3, 6 BY 19 ROEBLING SPECIAL SEALE

1¼	72-C	1.24	8.50	4.4	0	0	0	1.51	0.92	0.62	Aa	134,300	-----	0.593	226,000
1⅜	35-A	1.348	9.18	6.36	0	0	0	-----	1.00	.78	Db	136,600	100	.7680	177,000
	-B	1.339	9.40	6.16	0	0	0	2.05	.85	.70	Dc	131,800	97	.7230	182,000
	-C	1.294	10.14	6.22	0	0	0	1.82	.62	.68	Dc	140,500	103	.5990	234,000
1⅜	36-A	1.321	9.40	5.93	0	0	0	2.35	.84	.64	Dc	133,600	94	.7270	184,000
	-B	1.315	9.30	6.19	0	0	0	2.02	.75	.68	Dc	131,200	92	.6810	193,000
	-C	1.261	10.00	6.39	0	0	0	2.12	.60	.70	Dc	133,100	93	.5930	225,000

LAY, LANG, RIGHT—CONSTRUCTION 4, 6 BY 19 MODIFIED SEALE

1½	43-A	1.557	10.30	5.22	0	0	0	-----	1.00	0.80	Cb	213,000	100	0.9190	232,000
	-B	1.497	10.28	5.38	0	0	0	1.50	.87	.68	Ca	211,000	99	.8780	240,000
	-C	1.473	10.46	5.32	2	2	2	1.65	.79	.70	Ca	209,900	99	.8300	253,000

See footnotes at end of table.

TABLE 5.—*Results of inspection and tensile tests of worn wire ropes*—Continued

LAY, LANG, LEFT—CONSTRUCTION 4, 6 BY 19 MODIFIED SEALE

Nominal diameter	Rope	Diameter of measured rope	Rope lay	Strand lay	Number of broken wires in worst lay	Distribution of broken wires		Wear		Core		Rope			
						Strands [a]	Strands [b]	L	t/d	Diameter	Condition [c]	Breaking load	Remaining strength [d]	Remaining area	Tensile strength
in.		in.	in.	in.				in.		in.		lb	%	in.²	lb/in.²
1¼	12-A	1.779	11.74	7.20	0	0	0	-----	1.00	0.85	Da	241,300	100	1.266	190,000
	-Ba	1.700	11.68	6.78	0	0	0	1.94	.66	.80	Db	219,500	91	1.050	209,000
	-Bb	1.726	11.52	6.94	0	0	0	2.00	.80	.72	Db	242,700	101	1.164	209,000
	-Bc	1.670	11.68	6.82	0	0	0	1.81	.63	.82	Db	210,600	87	1.025	205,000
	-Bd	1.723	11.40	7.00	0	0	0	1.80	.74	.80	Db	216,300	90	1.118	193,000
	-C	1.685	11.66	6.94	27	6	4	1.80	.65	.73	Db	197,600	82	.960	206,000

[a] The number of strands having broken wires.
[b] The number of strands having 80 percent of the total number of broken wires.
[c] Core condition symbols:
For the lubrication of the core:
A=Well lubricated.
B=Fairly well lubricated.
C=Rather dry.
D=Dry.
E=Very dry.
For the condition of the fibers:
a=Long.
b=Some short.
c=Many short.
d=All short.
e=Rotted.
[d] The remaining strength is the ratio of the breaking load of the specimen to the breaking load of the specimen if there had been no wear and no broken wires.
[e] Three inside wires and core not broken. All others broken. Measurements of diameter and lay were made away from the break.
[f] These outside wire breaks were valley breaks. It is probable some inside wires were also broken.
[g] All outside wires and two inside wires of one strand were broken. The rope had been kinked.
[h] One strand was completely broken. No visible broken wires in remaining strands.
[i] All wires in one strand were broken plus other outside wires.
[j] One strand and about half of another were burned through, apparently by an electric arc. Other wires were doubtless decreased in strength.
[k] These are all outside wires.
[l] Five strands and core broken. No broken wires in remaining three strands.
[m] Some wires were locally crushed but apparently not worn.
[n] All wires in one outside strand were broken plus other outside wires.
[o] Wires of independent wire rope core somewhat rusty.
[p] The independent wire rope core was displaced.
[q] The broken wires were in the independent wire rope core; none was in the main rope.
[r] Wires rusty.
[s] All samples badly rusted and pitted.
[t] All samples badly rusted and pitted.

The following is a summary of the relation of the fracture in the rope to the worst lay. Of the ropes in which the worst lay could be definitely located, over 60 percent broke in the worst lay.

Total number of specimens for which the worst lay could be definitely located	124
Number of specimens C which broke in worst lay	57
Number of specimens C which broke within 12 inches of worst lay	8
Number of specimens C which broke more than 12 inches from worst lay	7
Number of specimens B which broke in worst lay	20
Number of specimens B which broke within 12 inches of worst lay	17
Number of specimens B which broke more than 12 inches from worst lay	12
Number of specimens A which broke in worst lay	2
Total number of specimens which broke in worst lay	79
Total number of specimens which did not break in worst lay	45

1. ROPE DIAMETER AND BREAKING LOAD

For a particular rope there usually was a decrease in diameter if there was a decrease in breaking load. Since the breaking load was decreased by broken wires which did not decrease the diameter of

the rope, a direct relation between diameter and breaking load was not to be expected. There appears to be no relation which holds for the different ropes. For example, for rope 53, the diameter of specimen C was 95.5 percent of that of specimen A, while the corresponding ratio of the breaking loads was 71.4 percent. On the other hand, for rope 6, the diameter of specimen C was 94.8 percent of that for specimen A, while the corresponding ratio of the breaking loads was 91.2 percent. In fact, table 5 gives values for remaining strengths (specimen C to specimen A) which range from less than 60 to 100 percent, with a corresponding decrease in rope diameter (specimen A to specimen C) of 5 percent.

It should, however, be pointed out that all the rope specimens A had been in use and under tension so that the measured diameters for specimens A were probably less than when these ropes were new.

2. ROPE AND STRAND LAY AND ROPE STRENGTH

For a particular rope there usually was an increase in the rope lay if there was a decrease in breaking load. However, the rope lay for specimen C was only a few percent greater than for specimen A. Again, it should be noted that all the specimens had been stretched by the service loading.

The strand lay did not vary consistently with variations in the breaking load for the different ropes.

3. CORE CONDITION AND ROPE STRENGTH

A study of the values given in table 5 does not indicate that there is any direct relation between either the diameter or the condition of the core and the breaking load.

For a particular rope there usually was considerably more lubricant in the core of specimen A than in the cores of specimens B and C. This was confirmed by the fact that, as the load on specimen A increased, considerable lubricant appeared on the surface of the rope. There appeared to be somewhat less lubricant in specimen C than in specimen B. The data in table 5 do not indicate any appreciable difference in the diameters of the cores in the three specimens from the same rope. This diameter could not be measured very accurately, which may be the reason that measurements were obtained which show that the diameter of the core of specimen C is sometimes greater than that of specimens A and B.

For most of the ropes the fibers in the cores of specimen C were shorter than those in specimen B. Those in specimens B and C were shorter than those in specimen A.

In most cases, the cores having little lubricant and the shortest fibers were found in the specimens having the most wear and the greatest number of broken wires. This made it impossible to determine the effect of the core upon the breaking load.

4. REMAINING AREA AND ROPE STRENGTH

If the breaking load of a worn wire rope depends only on the remaining area of the wires, then the ratio of the breaking load to the remaining area should be constant for all specimens from a given rope. This ratio is the tensile strength (lb/in.^{2}), the values for which are given in table 5.

In some cases the tensile strength for specimen C is greater and in some cases less than for specimen A. It is probable that these differences are caused by the distribution of broken wires in specimen C. Table 6 gives the number of ropes for which the tensile strength of specimen C was greater or less than that of specimen A. Only six-strand ropes showing no corrosion were selected when preparing this table. Definite conclusions should not be drawn from the results obtained on only 40 ropes. There are indications that, if the tensile strength of specimen C was greater than that of specimen A, the broken wires were quite uniformly distributed; that is, there were broken wires in four or more of the strands. If the tensile strength of specimen C was less than that of specimen A, the broken wires were not uniformly distributed; that is, there were broken wires in only one, two, or three of the strands. In other words, the more uniform the distribution of the broken wires,the greater the tensile strength.

TABLE 6.—*Comparison of breaking loads for specimens C and A of six-strand ropes showing no corrosion*

[Specimen A had no wear and no broken wires]

Breaking load	Number of strands of specimen C having broken wires						
	0	1	2	3	4	5	6
Specimen C greater than specimen A (number of ropes)	3	1	2	4	4	6	2
Specimen C less than specimen A (number of ropes)	0	3	9	2	3	1	0

For those ropes in which one or two strands had most of the broken wires (80 percent or more)—that is, the broken wires were not uniformly distributed—the tensile strength for specimen C was usually less than for specimen A. It appears then that if the broken wires are not uniformly distributed among the strands the remaining area cannot safely be used as a criterion of the strength of the rope. Some fractional part of the remaining area (to be determined from the results of a large number of tests) might be satisfactory. It is probable that the effect of the distribution of the broken wires on rope strength extends to the distribution of the broken wires in each strand. This conclusion is supported by the data of table 6, since for some ropes specimen C had a smaller tensile strength than specimen A when there were broken wires in four and five strands.

The same effect of the distribution of the broken wires was found by comparing the tensile strength of the B specimens and the A specimens. The indication, however, was less definite because the B specimens had comparatively few broken wires.

5. CORROSION

Corrosion of the wires decreases their cross-sectional area. The actual cross-sectional area of a corroded wire rope, therefore, may be much less than the remaining area determined from the number of broken wires and the amount of wear. Probably the strength of a corroded wire rope can only be determined by a tensile test of a specimen cut from the rope.

6. THE BREAKING LOADS OF SPECIMENS C AND A

Specimen C was supposed to have been taken from the portion of the rope which was in the poorest condition and which was supposedly used by the inspector in determining when the rope should be discarded. For the ropes received, figure 10 shows the number of ropes

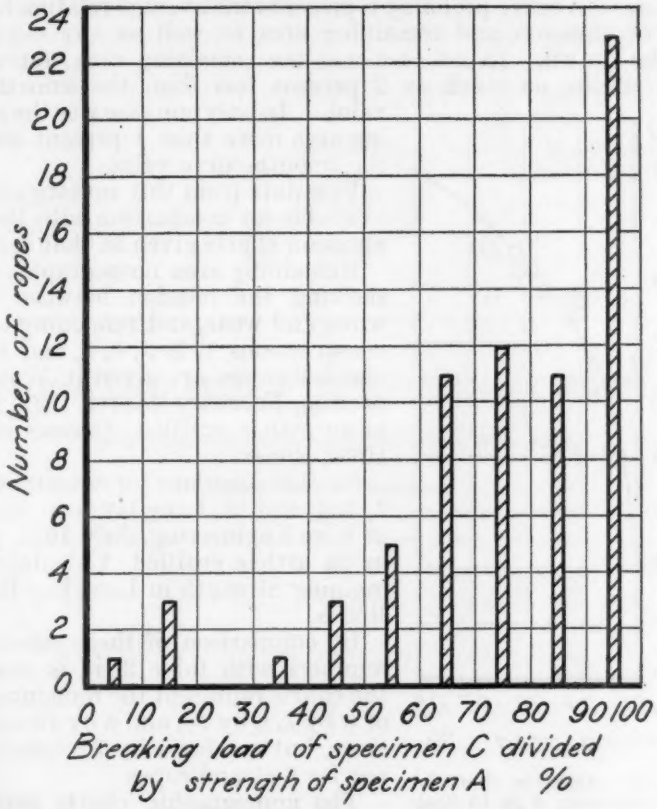

FIGURE 10.—*Relative strengths of specimens* C *and* A.

in comparison with the relative strengths of specimens C and A. Forty-nine percent of these discarded ropes had a strength for specimen C, which was at least 80 percent of that for specimen A.

VI. COMPARISON OF RESULTS WITH ROEBLING CHARTS

1. THE ROEBLING CHARTS

The strength of worn wire ropes is discussed in Wire Engineering, June–July 1931, page 7, in an article entitled Re-Roping Charts. In this article are shown curves giving the relation between length of abrasion and the remaining area for a few types and diameters of ropes. Among these charts is chart 6 for ⅝ inch diameter, 6 by 19 Seale, Roebling Special Traction Steel Rope, Construction 2. Table

3 of this report shows that 48 specimens of this size and construction were included in this investigation. Some of these ropes were not manufactured by this company. The remaining area and length of abrasion for these 16 lots of rope have been plotted in figure 11, as has the smooth curve which was taken from chart 6 of the article, Re-Roping Charts. While a few erratic values are shown in figure 11, the smooth curve probably represents the average relation between length of abrasion and remaining area as well as any curve that might be drawn. In no case was the remaining area, represented by the circles, as much as 2 percent less than the smooth-curve value. In only one case was the remaining area more than 1 percent less than the smooth-curve value.

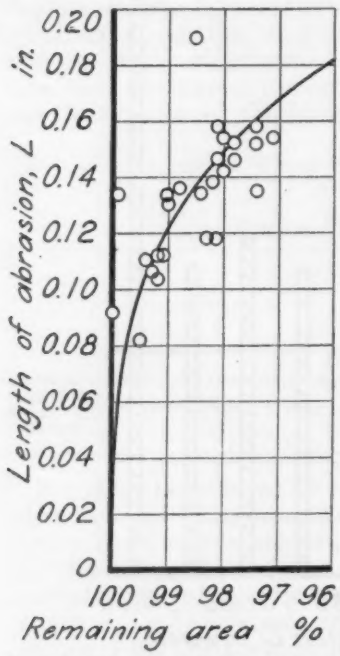

FIGURE 11.—*Abrasion chart for 5/8-inch diameter, 6 by 19 Seale construction 2, wire ropes.*

The smooth curve was taken from chart 6, Wire Engineering, p. 18, June-July 1931.

Few data from this investigation are available for comparison with the other abrasion charts given in that article.

Remaining area nomographic charts, showing the relation between broken wires and wear, and remaining area for constructions 1, 2, 3, 4, 5, and 18, regular lay ropes, are given in Wire Engineering, February–March 1932, page 2, in an article entitled, Stresses in Shaft Hoist Ropes.

Similar diagrams for constructions 1, 2, 3, 4, and 18, Lang lay rope, are given in Wire Engineering, July 1932, page 2, in an article entitled, Calculating Remaining Strength in Lang Lay Hoisting Ropes.

By comparison of these construction numbers with table 2, it is seen that the charts represent the remaining areas of 6 by 7, 6 by 16, and 6 by 19 constructions, but not for 6 by 37 construction nor for 8 strand ropes.

The nomographic charts pertaining to the rope constructions represented by these tests, copied from those given in the articles in Wire Engineering, are given in this report in figures 12 to 22, inclusive. The procedure in using these charts is as follows:

Draw a line from the rope diameter on scale A through the average length of wear L or Q on scale "B" to intersect scale C. At this intersection read the percentage of the wire diameter remaining. Connect this percentage of the wire diameter remaining on scale D to the number of broken wires in the worst rope lay on scale F and read the percentage of the rope area remaining intact at the intersection on scale E.

Reference has been made to the effect of the distribution of broken wires in the various strands on the tensile strength of the rope and the necessary correction to the remaining rope area if the distribution is not uniform. The Roebling wire engineers have found, from

PARALLEL SCALE COMPUTING GRAPHS

For Computing the Strength of Worn Wire Rope

Figures 12 to 22, inclusive

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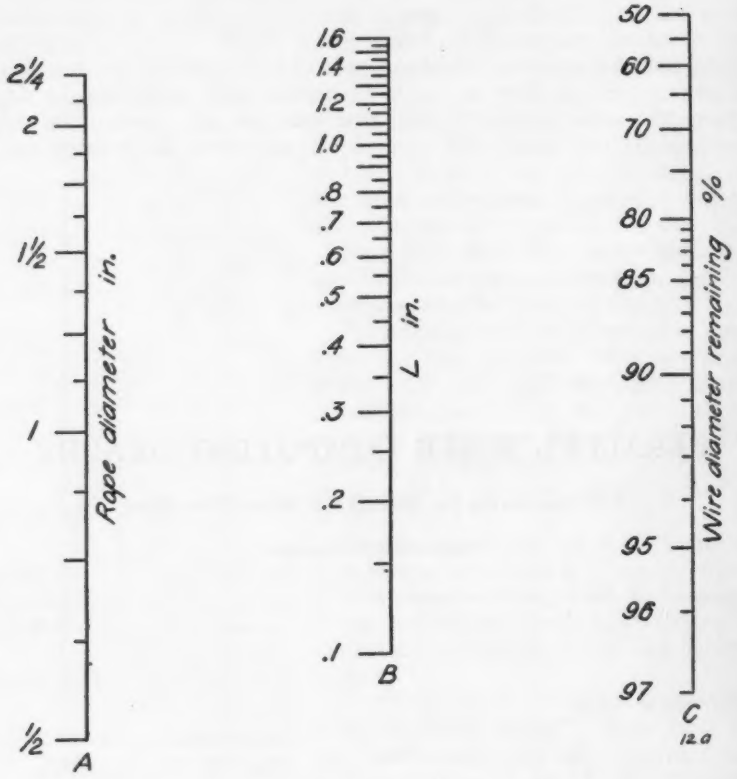
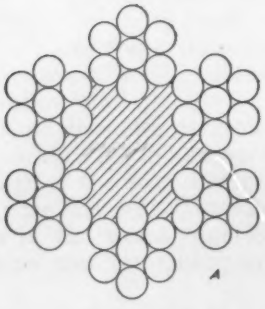

2¼
2
1½
1
½
A
Rope diameter in.
1.6
1.4
1.2
1.0
.8
.7
.6
.5
.4
.3
.2
.1
B
L in.
50
60
70
80
85
90
95
96
97
C
Wire diameter remaining %
12.0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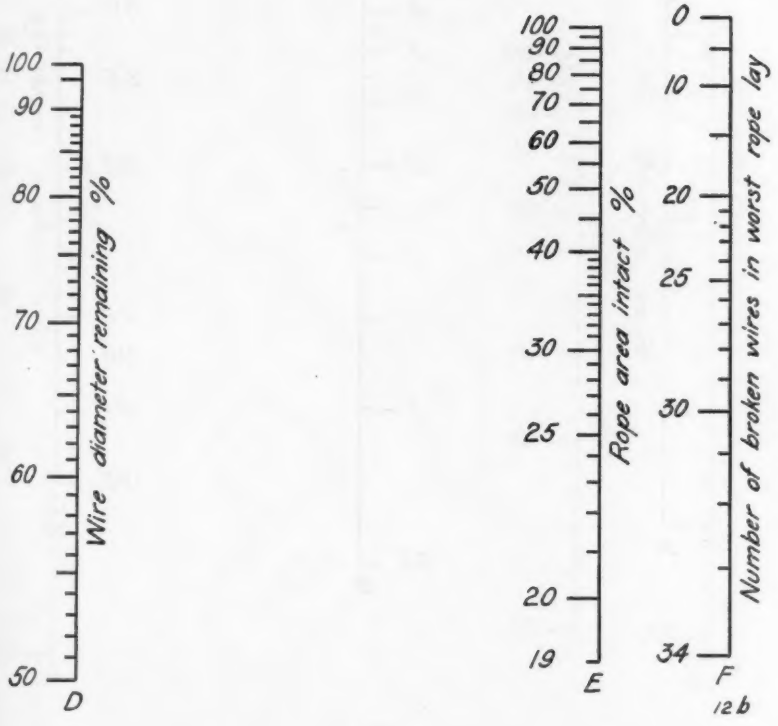
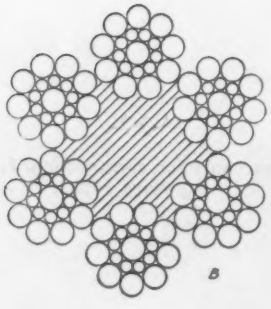


FIGURE 12.—*Remaining area chart for construction 1, 6 by 7 coarse laid, regular lay wire rope.*

2¼
2
1½
1
½
A
Rope diameter in.
1.4
1.2
1.0
.8
.7
.6
.5
.4
.3
.2
.1
.05
B
L in.
50
60
70
80
85
90
95
96
97
98
C
Wire diameter remaining %

13a



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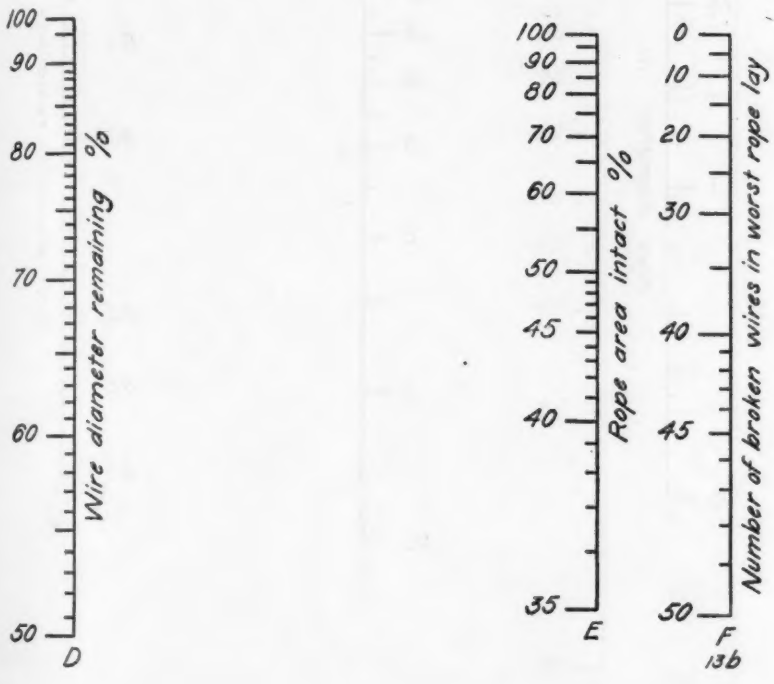
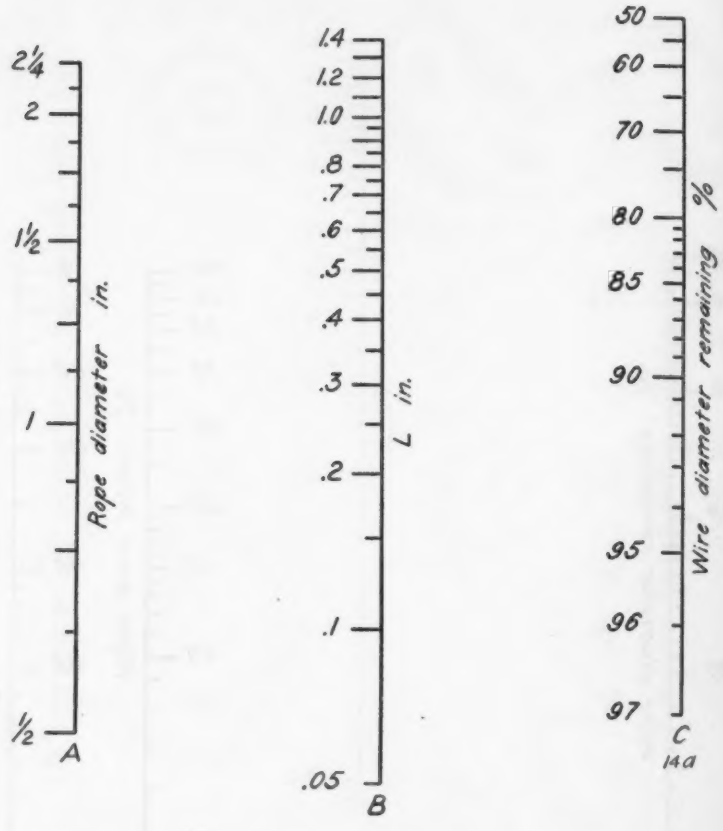


FIGURE 13.—*Remaining area chart for construction 2, 6 by 19 Seale, regular lay wire rope.*


2¼
2
1½
1
½
Rope diameter in.
A
1.4
1.2
1.0
.8
.7
.6
.5
.4
.3
.2
.1
.05
L in.
B
50
60
70
80
85
90
95
96
97
Wire diameter remaining %
C
14a

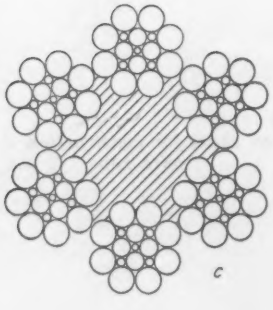

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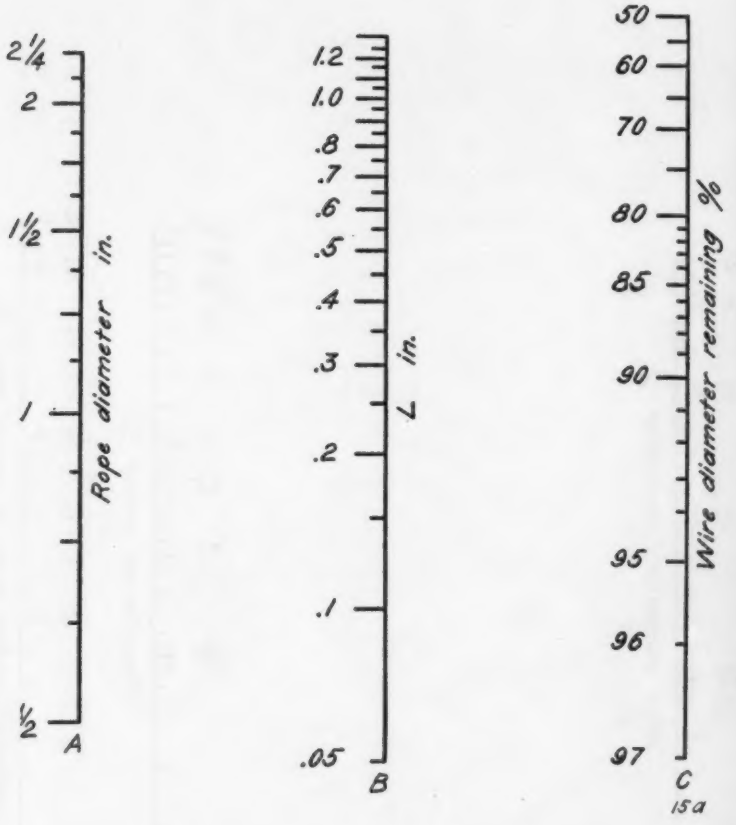
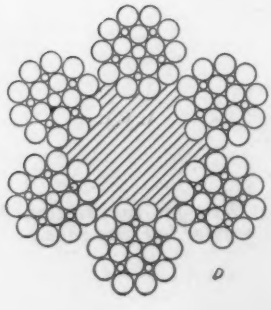
FIGURE 14.—*Remaining area chart for construction 18, 6 by 16 special Seale, regular lay wire rope.*


2¼
2
1½
1
½
A
Rope diameter in.
1.2
1.0
.8
.7
.6
.5
.4
.3
.2
.1
.05
B
L in.
50
60
70
80
85
90
95
96
97
C
Wire diameter remaining %

15a



D

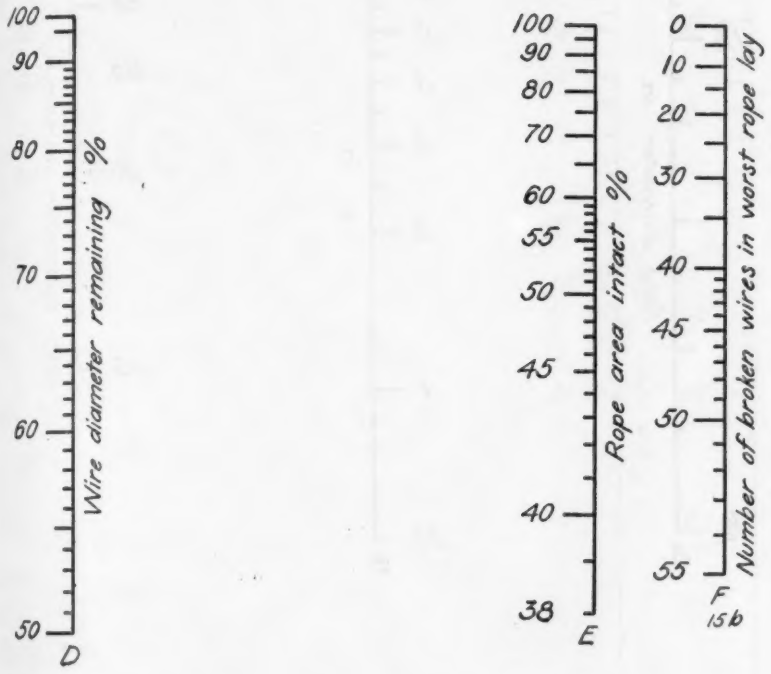
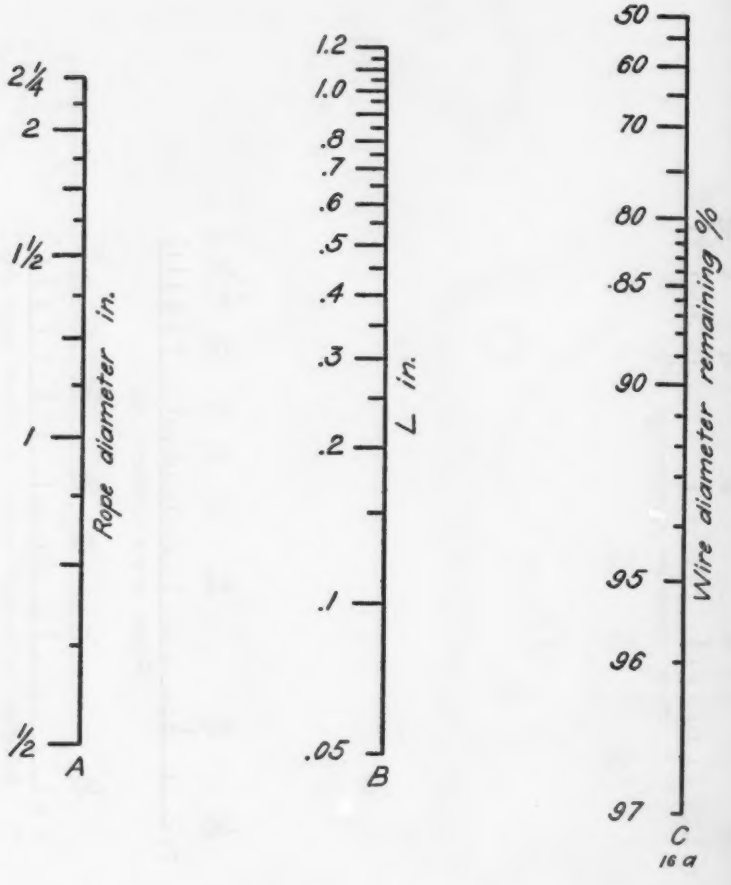


FIGURE 15.—*Remaining area chart for construction 3, 6 by 19 Roebling special Seale, regular lay wire rope.*


2¼
2
1½
1
½
Rope diameter in.
A
1.2
1.0
.8
.7
.6
.5
.4
.3
.2
.1
.05
L in.
B
50
60
70
80
85
90
95
96
97
Wire diameter remaining %
C
16 a

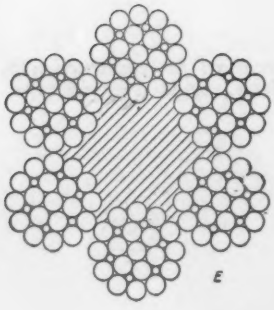
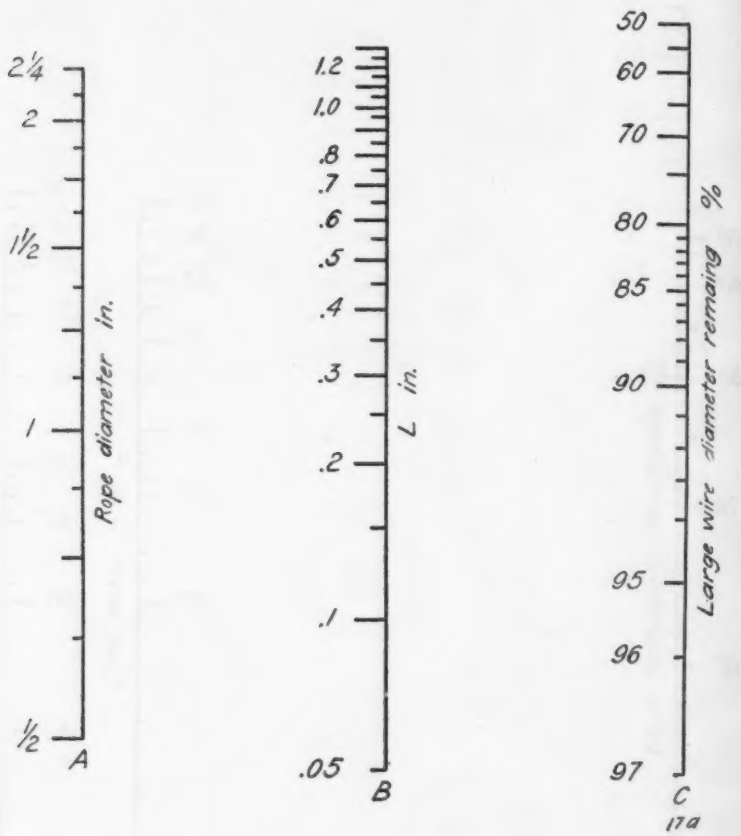
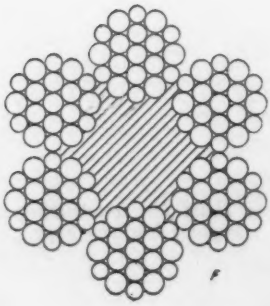

E

FIGURE 16.—*Remaining area chart for construction 4, 6 by 19 modified Seale, regular lay wire rope.*


2¼
2
1½
1
½
Rope diameter in.
A
1.2
1.0
.8
.7
.6
.5
.4
.3
.2
.1
.05
L in.
B
50
60
70
80
85
90
95
96
97
Large wire diameter remaing %
C

17a



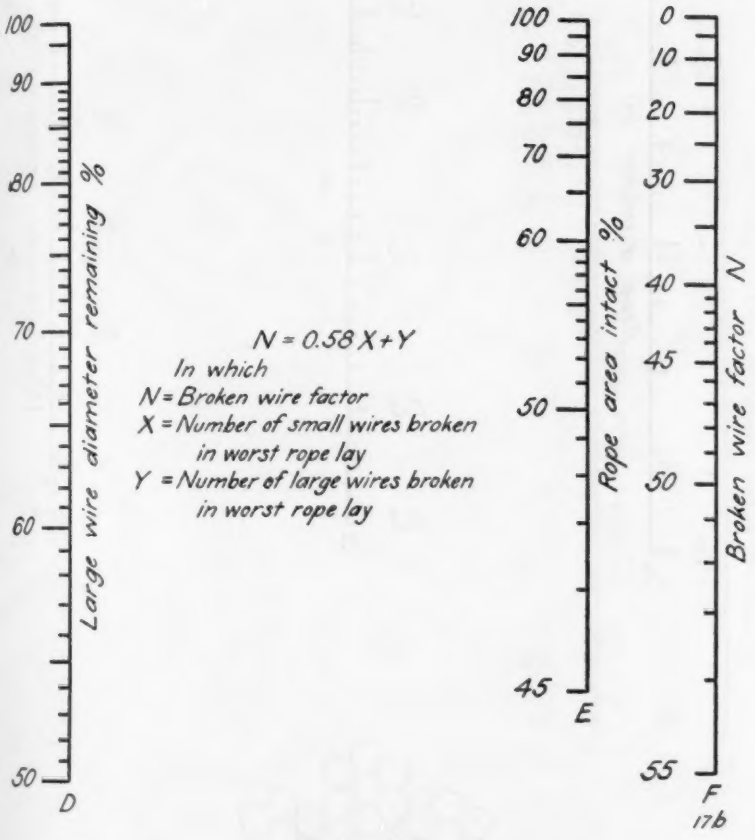
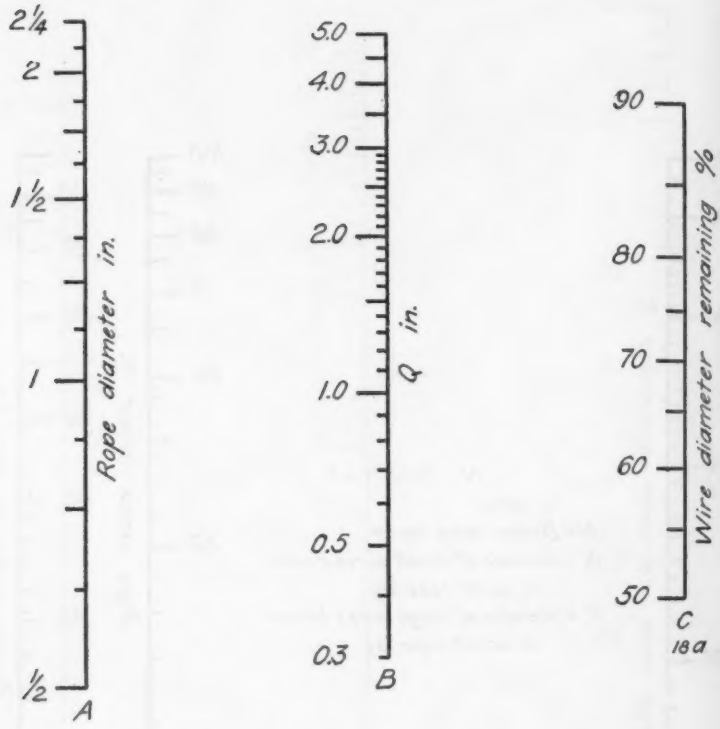
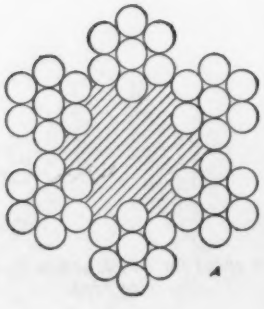


FIGURE 17.—*Remaining area chart for construction 5, 6 by 19 Warrington, regular lay wire rope.*


2¼
2
1½
1
½
Rope diameter in.
A
5.0
4.0
3.0
2.0
1.0
0.5
0.3
Q in.
B
90
80
70
60
50
Wire diameter remaining %
C
18a



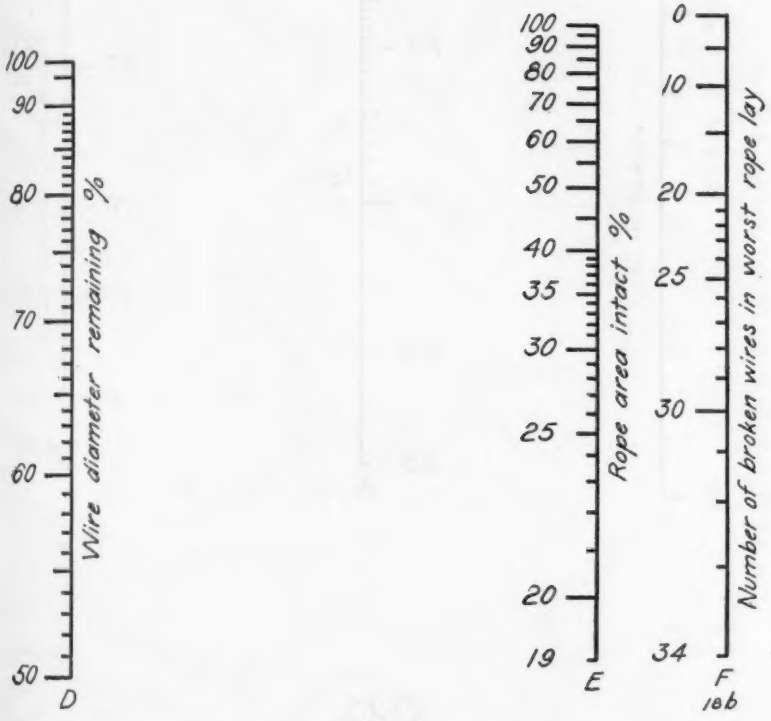
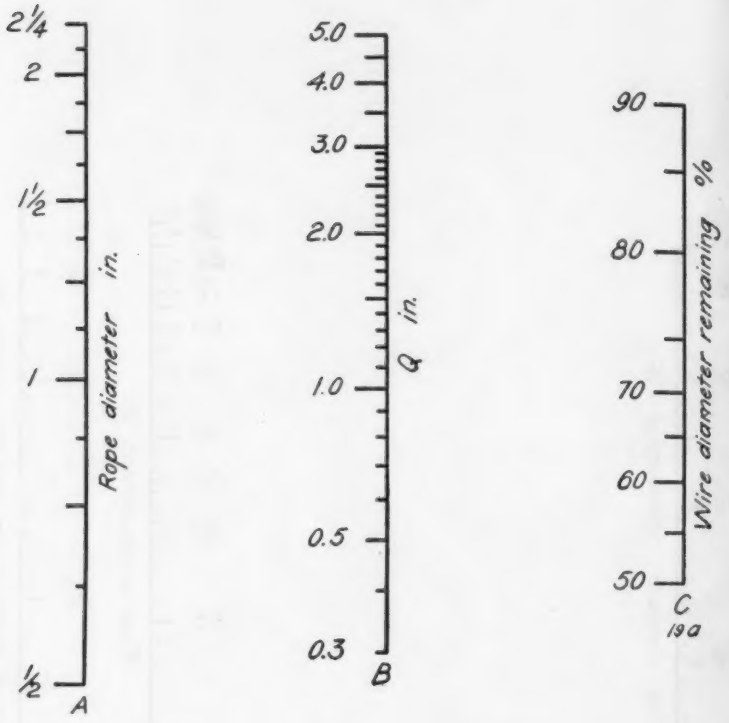
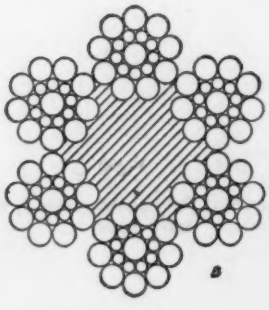


FIGURE 18.—*Remaining area chart for construction 1, 6 by 7 coarse laid, Lang lay wire rope.*


2¼
2
1½
1
½
Rope diameter in.
A
5.0
4.0
3.0
2.0
1.0
0.5
0.3
Q in.
B
90
80
70
60
50
Wire diameter remaining %
C
190



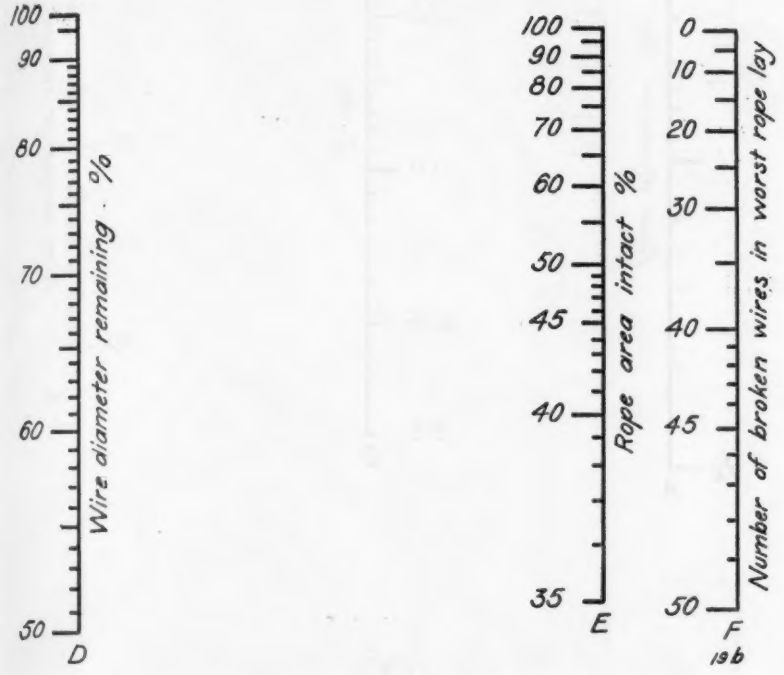
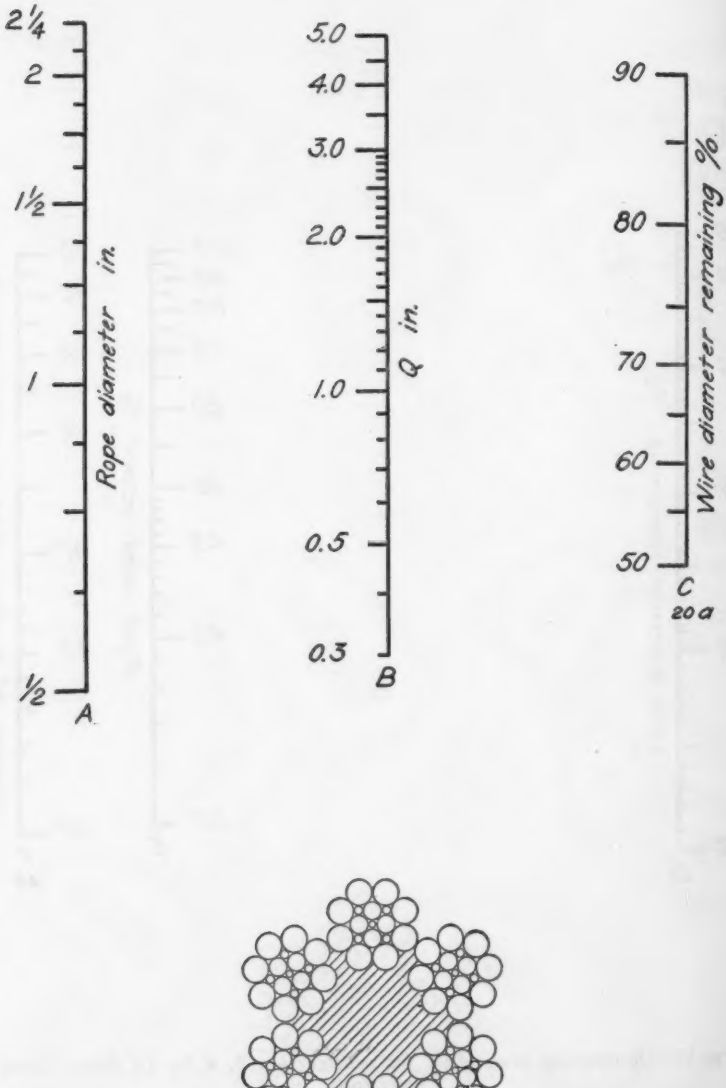
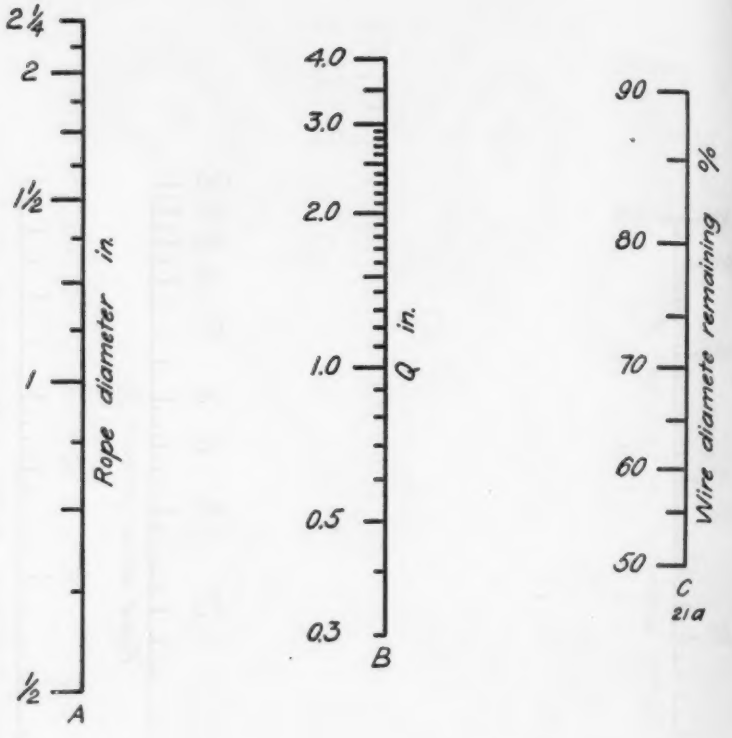


FIGURE 19.—*Remaining area chart for construction 2, 6 by 19 Seale, Lang lay wire rope.*

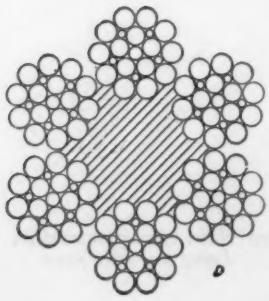

2¼
2
1½
1
½
Rope diameter in.
A
5.0
4.0
3.0
2.0
1.0
0.5
0.3
Q in.
B
90
80
70
60
50
Wire diameter remaining %
C
20 a

c

FIGURE 20.—*Remaining area chart for construction 18, 6 by 16 special Seale, Lang lay wire rope.*


2¼
2
1½
1
½
A
Rope diameter in.
4.0
3.0
2.0
1.0
0.5
0.3
B
Q in.
90
80
70
60
50
C
Wire diameter remaining %

21a



b

FIGURE 21.—*Remaining area chart for construction 3, 6 by 19 Roebling special Seale, Lang lay wire rope.*

2 1/4
2
1 1/2
1
1/2
Rope diameter in.
A
4.0
3.0
2.0
1.0
0.5
0.3
Q in.
B
90
80
70
60
50
Wire diameter remaining %
C
22a

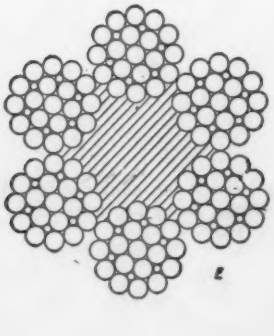

t

FIGURE 22.—*Remaining area chart for construction 4, 6 by 19 modified Seale, Lang lay wire rope.*

a large number of experiments, that the effective remaining area, allowing for the distribution of broken wires, is related to the remaining area found from calculations of the number of wires unbroken and wear on the outside wires, as shown in figure 23. In making a correction, allowing for the distribution of broken wires, the number of strands considered as having broken wires has been taken as the number of strands having 80 percent of the total number of broken wires (see table 5). If the total number of strands which had any broken wires (frequently only one or two wires in some strands) is considered, the decrease in effective area due to the distribution of broken wires, is probably not fully indicated by figure 23.

2. ROPE STRENGTHS INDICATED BY THE CHARTS

Since the strengths of the wire ropes, when new and unused, submitted for these tests are not known, it has been necessary to make comparisons between the strength of the specimen least worn and of those which had broken wires or wear. For those ropes for which specimen A had no visible wear or broken wires, the area of specimen A, as well as the strength, has been considered to be 100 percent. For the ropes for which specimen A had either wear or broken wires the area of an assumed specimen having no wear or broken wires was calculated, and the strength of specimen A was considered to be in the same proportion to that of the assumed specimen as the relative areas.

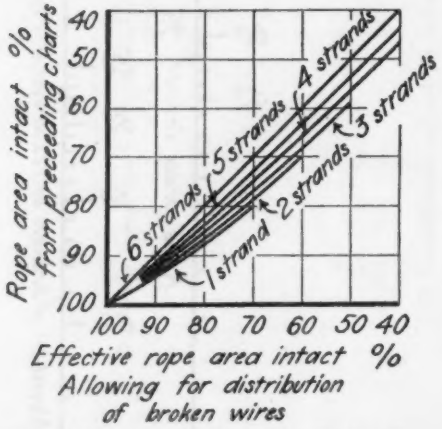


FIGURE 23.—*Remaining area, effective allowing for distribution of broken wires.*

From the remaining area charts and from figure 23 the percentage of the rope area intact was found for all specimens for which charts were available. The strength of the specimens B and C of each rope was then calculated from the remaining effective area and the strength of specimen A.

3. COMPARISON OF TEST RESULTS AND CHART VALUES

The relation between the actual breaking load and the values obtained from the charts is shown in figures 24 and 25. The 45-degree line in these figures obviously represents the condition for which these values would be equal. These figures show that, for most ropes, the actual breaking load was somewhat greater than the values obtained from the charts. Of 109 specimens (specimens B and C) available for comparison, 19 specimens are shown in these figures for which the actual breaking load was less than the chart value. Data for these specimens are given in table 7.

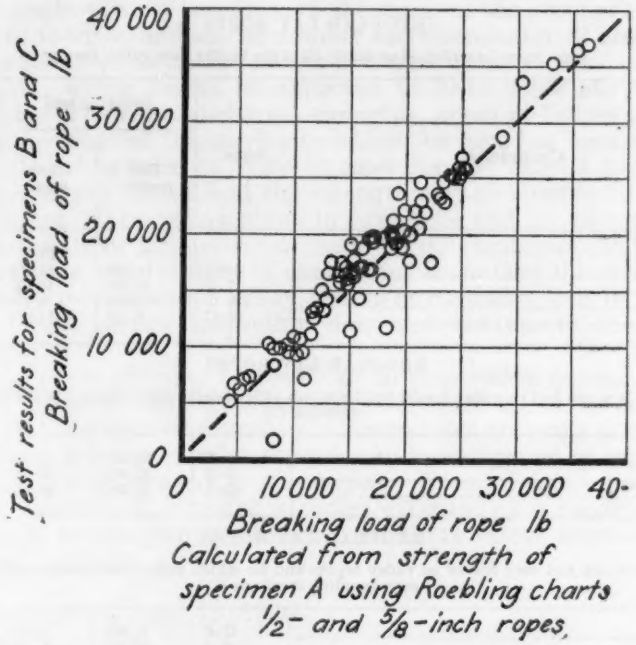


FIGURE 24.—*Relation between the actual breaking load and the values obtained from the charts for ½- and ⅝-inch diameter ropes*

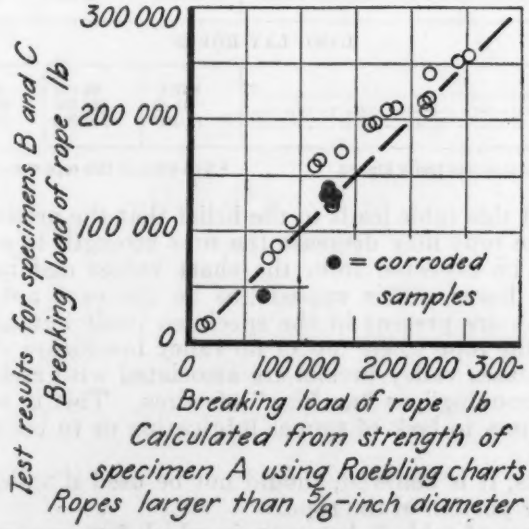


FIGURE 25.—*Relation between the actual breaking load and the values obtained from the charts for ropes having a diameter larger than ⅝ inch*

TABLE 7.—*Ropes for which the breaking load was less than the chart value*

REGULAR LAY ROPES

(Specimens in which all or nearly all of the breaks were valley breaks)

Construction	Rope	Breaking load		Difference between actual and chart value—percentage of chart value
		Test results	Chart value	
		lb	lb	%
2	69–C	11,500	15,000	23
5	17–B	9,300	10,700	13
5	58–C	[a] 1,900	8,150	77
5	62–C	7,100	11,000	36

REGULAR LAY ROPES

(Specimens B which had no valley breaks but for which valley breaks predominated in the corresponding specimen C)

2	8–B	22,950	23,500	2
2	38–B	17,500	22,200	20
5	62–B	11,600	18,400	37

REGULAR LAY ROPES

(Specimens which had very few or no valley breaks and for which valley breaks were not found in the corresponding specimen C)

2	37–C	17,850	19,600	9
2	40–B	20,600	21,300	3
2	44–B	20,050	20,300	1
2	44–C	17,750	20,300	13
2	53–C	11,200	11,300	1
2	71–C	15,800	18,000	12
5	18–C	20,250	20,400	1
5	23–B	14,350	15,800	10
5	68–2–B	9,500	10,600	10

LANG LAY ROPES

1	[b] 31–C	44,000	67,400	35
2	11–C	122,700	126,000	3
4	12–BC	210,600	212,200	1

[a] This rope was badly kinked.

[b] The wires of this rope were rusty.

A study of this table leads to the belief that the presence of valley breaks in the rope may decrease the rope strength to a value lower than would be expected from the chart values and in some cases dangerously lower. This appears to be the case not only where valley breaks are present in the specimen itself but also for other portions of the rope where few or no valley breaks are visible.

In many cases valley breaks are associated with and are a direct result of "grooving" or "necking" of wires. This is attributed by some inspectors to lack of proper lubrication or to too small sheave diameters.

The charts, it is believed, should not be used if valley breaks are found in any portion of the rope.

In the ropes of table 7, however, in which few or no valley breaks were present, the actual breaking load was less than the chart value by a relatively small amount. Except for rope 31–C, which was corroded, 13 percent was the greatest difference.

The computed rope strength (chart value) depends on the strength of the single unworn specimen of the rope, on the amount of wear on the outside wires, and on the number and distribution of broken wires. It does not depend on the abrasion of the inside wires or on the core condition, which might be expected to have some effect on rope strength. The computed rope strengths, given in figures 24 and 25, take no account of the service to which the rope has been subjected, although the articles in Wire Engineering are careful to point out that the service does affect the strength and give corrections for elevator ropes. The values given in figures 24 and 25, however, based on the results of tests of ropes made by different manufacturers and used under a wide variety of conditions, show that the strength of a worn wire rope, without valley breaks or corrosion, can be estimated closely from surface inspection data and the use of the Roebling charts.

If the ropes showing corrosion or having valley breaks are disregarded, there remain only a few ropes for which the test results do not agree with the computed values. These cases are not a large proportion of the total number of ropes for an investigation of structures as varied and complicated as wire ropes. None of these discrepancies (valley break and corroded samples excepted) are considered large enough to be dangerous, provided the chart values showed the rope to have been safe.

WASHINGTON, April 13, 1936.

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RESEARCH PAPER RP921

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EBULLIOMETRIC AND TONOMETRIC MEASUREMENTS ON NORMAL ALIPHATIC HYDROCARBONS

By Mieczysław Wojciechowski[1]

ABSTRACT

By the application of the precise method developed by W. Swietoslawski for measuring the boiling points and the differences between boiling point of liquids and the condensation temperature of their vapors, it is possible to determine several facts of interest to the chemist. Among these are the purity of the substance under investigation, its boiling point, and the relation of boiling point to pressure.

The normal hydrocarbons, pentane, hexane, heptane, and octane have been studied by this method. The ebulliometric control of purity of the preparations, the use of substances of high purity, and the application of a method of comparative measurements insure the accuracy of the results reported.

The numerical data are as follows: *n*-pentane, boiling point 36.077, $\frac{dt}{dp}=0.0391$; *n*-hexane, boiling point 68.733, $\frac{dt}{dp}=0.0420$; *n*-heptane, boiling point 98.365, $\frac{dt}{dp}=0.0449$; *n*-octane, boiling point 125.658, $\frac{dt}{dp}=0.0477$.

It was found that the introduction of a CH_2 group into the chain of each of the normal aliphatic hydrocarbons investigated has the specific effect of increasing the $\frac{dt}{dp}$ ratio by the amount 0.0029.

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I. INTRODUCTION

The development of W. Swietoslawski's precise ebulliometric technic[2] and application of the comparative method of measurements[3] offers an opportunity for systematic ebulliometric and tonometric studies. The present work was done to establish exact data

[1] Guest worker from Polytechnic Institute, Warsaw, Poland.
[2] W. Swietoslawski, Ebuljometrja, Warszawa (1935).
[3] W. Swietoslawski, J. chim. phys. 27, 496 (1930), Roczniki Chem. 9, 266 (1929).

on boiling points and $\frac{dt}{dp}$ ratios, the rate of change of boiling point with change of pressure, as well as to investigate the relation between the *constitution* of a compound, and the value of its $\frac{dt}{dp}$ ratio for a series of normal aliphatic hydrocarbons.

The application of the sensitive ebulliometric test for purity makes it possible to select preparations of high purity and consequently to obtain results which approach very closely to the constants for substances of "absolute" purity.

II. METHOD OF MEASUREMENT

The method of measurement used in the present work has been described in detail by W. Swietoslawski.[4] The following are the principles of the method. A barometric ebulliometer [5] filled with water as a reference liquid, and a standard differential ebulliometer,[6] containing the substance under investigation, are connected to a manostat, and the boiling point of each liquid is measured at three or more different pressures. The ratio of the change in boiling point of the given substance to the change in the boiling point of water caused by the change in pressure is equal to the ratio between the $\frac{dt}{dp}$ coefficients of the given substance and that of water.

$$\frac{dt_s}{dt_w}=\frac{\frac{dt}{dp_s}}{\frac{dt}{dp_w}}$$

A. Zmaczynski [7] has carefully investigated the influence of pressure on the ratio $\frac{dt_s}{dt_w}$ for several substances, and found that the curve representing this relation has only a very small curvature and a relatively small slope, thus permitting interpolation of the data to the pressure at which the boiling point was determined.

Obviously, the correction for pressure to be introduced in calculating the normal boiling point of the substance investigated is equal to the correction for water multiplied by the ratio $\frac{dt_s}{dt_w}$. In this manner the boiling point of water serves as a barometric reading, and gives directly the value of the correction to normal pressure as the difference 100—t'_w, where t'_w is the boiling point of water actually measured.

The normal boiling point t_s of the substance under investigation may be calculated by the formula

$$t_s=t'_s+\frac{dt_s}{dt_w}(100-t'_w)$$

[4] W. Swietoslawski, J. Chim. phys., also A. Zmaczynski, Roczniki Chem. **13**, 181 (1933); J. chim. phys. **27**, 503 (1930).
[5] W. Swietoslawski, Bul. int. Acad. Polonaise [A] **1929**, 434; Bul. Soc. Chim. France **49**, 1563; Z. phys. Chem. [A] **160**, 257 (1932).
[6] W. Swietoslawsi, I X Congreso Int. Quim. Pura Aplicada, Madrid **1934**, 13; J. Phys. Chem. **38**, 1109 (1935); Z. phys. Chem. [A] **160**, 257 (1932).
[7] A. Zmaczynski, J. chim. phys. **27**, 503 (1930); Roczniki Chem. **13**, 181 (1933).

where t'_s is the boiling point of the substance actually measured under the same pressure as t'_w, that of water.

A knowledge of the ratio $\frac{dt_s}{dt_w}$ for the given substance permits calculation of the value of the $\frac{dt}{dp}$ ratio, referred to that of water as the primary reference liquid.

$$\frac{dt}{dp_s}=\frac{dt}{dt_w}\frac{dt_s}{dp_w}$$

This method permits rapid and precise measurements of $\frac{dt}{dp}$ ratios. The value 0.0370 for $\frac{dt}{dp}$ of water at normal pressure, found by Zmaczynski and Bonhour,[8] was used in calculating the $\frac{dt}{dp}$ ratios reported in this paper.

III. CONTROL OF PURITY OF SUBSTANCES

Swietoslawski's ebulliometric test [9] for the purity of liquid substances, as used in this work, is based on the measurement of Δt, the difference between the boiling and condensation temperatures in an ebulliometer of standard dimensions. For a pure substance or an azeotropic mixture, this difference is equal to zero, and increases with concentration of impurities. The magnitude of Δt depends also on the nature of the impurities.

To classify the purity of the preparations under investigation, Swietoslawski's scale of purity of liquid substances was used. According to this scale, substances are divided into five groups, as shown below.

Limits of Δt	Degree of purity
°C	
0.000 to 0.005	V
.005 to .020	IV
.020 to .050	III
.050 to .100	II
.100 to 1.000	I

IV. MEASUREMENTS OF TEMPERATURE

Boiling points were measured with a potential terminal platinum resistance thermometer with coiled filament,[10] calibrated at this Bureau, and kindly furnished by C. H. Meyers. The measurements of the degree of purity were made with a Beckmann-Swietoslawski mercury thermometer.[11]

[8] A. Zmaczynski and A. Bonhour, J. Phys. **1**, 285 (1930).
[9] W. Swietoslawski, IX Congreso Int. Quim. Pura Aplicada, Madrid **1934**, 13.
[10] C. H. Meyers, BS J. Research **9**, 807 (1932) RP508.
[11] W Swietoslawski, Roczniki Chem. **11**, 545 (1931).

V. METHOD OF EXTRAPOLATION OF THE BOILING POINT

To calculate the normal boiling point of a substance not of high purity, a method of extrapolation related to that previously reported[12] was applied. The method is based on the correlation of the change of boiling point with the change of Δt, the difference between the boiling point and condensation temperature, when distilling through the side tube of the ebulliometer successive small portions, each of a few milliliters, of the preparation. This distillation partially removes the more volatile impurities, and the substance then behaves like a series of preparations containing different amounts of practically the same kind of impurities. By plotting boiling point T, T_1, T_2 . . . . against corresponding differences Δt, Δt_1, Δt_2 . . . one may easily extrapolate to the boiling point of the preparation having the difference Δt equal to zero, which is the boiling point of the pure substance.

VI. MATERIALS USED

In the present work there have been investigated the following hydrocarbons: *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane.

1. *n*-PENTANE

The *n*-pentane used was that prepared synthetically and purified by Mair.[13] The sample used had a difference between the boiling and condensation temperatures of 0.002° C, and was accordingly of the fifth (highest) degree of purity on Swietoslawski's scale.

2. *n*-HEXANE

Two preparations of *n*-hexane were used. One was prepared synthetically and purified by Mair;[14] the other was also synthetic. Mair's preparation, having Δt equal to 0.005° C, was of the fifth degree of purity. The second preparation investigated was of the fourth degree of purity, as indicated by a value of 0.010° C for Δt.

3. *n*-HEPTANE

A preparation of *n*-heptane obtained from Mair, distilled from Jeffrey pine oil, was used. This preparation, having a difference Δt between its boiling point and temperature of condensation equal to 0.013° C, was according to Swietoslawski's scale of the fourth degree of purity.

Another preparation of *n*-heptane from Jeffrey pine oil, purified by distillation in a locket chain column by F. W. Rose, Jr., was of the fifth degree of purity, having Δt equal to 0.005° C.

4. *n*-OCTANE

The preparation of *n*-octane used was prepared by B. J. Mair, and was found to be of the fourth degree of purity, having Δt=0.008° C.

[12] M. Wojciechowski and E. R. Smith, Nature **138**, 30 (1936).
[13] B. J. Mair, BS J. Research **9**, 457 (1932) RP482.
[14] See footnote 13.

VII. EXPERIMENTAL RESULTS AND CONCLUSIONS

The data on boiling points obtained in the present work are tabulated in table 1.

TABLE 1.—*Boiling points of four normal aliphatic hydrocarbons*

Substance	Δt	Degree of purity	Boiling point	Boiling point extrapolation
	°C		°C	°C
n-Pentane	0.002	V	36.077	
n-Hexane	.005	V	68.733	
	.010	IV	68.679	
n-Heptane	.013	IV	98.345	98.364
	.005	V	98.365	
n-Octane	.008	IV	125.655	125.658

In table 2 results for boiling points and $\frac{dt}{dp}$ ratios previously reported by other authors are compared with those given in table 1.

TABLE 2.—*Comparison of the data with those of other observers*

Observer	n-Pentane		n-Hexane		n-Heptane		n-Octane	
	Boiling point	$\frac{dt}{dp}$ p=760	Boiling point	$\frac{dt}{dp}$ p=760	Boiling point	$\frac{dt}{dp}$ p=760	Boiling point	$\frac{dt}{dp}$ p=760
	°C		°C		°C		°C	
Mair	36.06		68.70		98.38		125.59	
Shepard, Henne, and Midgley	36.00		68.71	0.042	98.38	0.045	125.59	0.048
Timmermans and Martin			68.80	0.42 (10 mm of Hg)			125.8	.47 (10 mm of Hg)
Timmermans	36.10	0.41 (10 mm of Hg)			98.35	.45 (10 mm of Hg)		
Young	36.3	.0388			98.43	.045		
Woringer			68.53	.418			124.32	.0478
Author	36.07[7]	.0391	68.73[8]	.0420	98.36[8]	.0449	125.65[8]	.0477

Table 3 contains the tabulated values of $\frac{dt_s}{dp_w}$ and $\frac{dt}{dp}$ ratios for the four hydrocarbons.

TABLE 3.—*Data on* $\frac{dt_s}{dt_w}$ *and* $\frac{dt}{dp}$ *ratios for four normal aliphatic hydrocarbons*

Substance	$\frac{dt_s}{dt_w}$	Corresponding temperature	$\frac{dt}{dp_{p=760}}$	Difference in $\frac{dt}{dp}$ ratios
		°C		
n-Pentane	1.0654	100.836	0.0391	
	1.0407	98.032		0.0029
n-Hexane	1.1383	101.075		
	1.1324	97.948	.0420	
	1.1271	94.035		.0029
n-Heptane	1.2149	100.820		
	1.2136	98.029	.0449	
				.0028
n-Octane	1.2976	100.895		
	1.2708	97.877	.0477	

From table 3 it is apparent that the introduction of a CH_2 group into the chain of the normal aliphatic hydrocarbon has a specific effect, increasing the $\frac{dt}{dp}$ ratio by a constant value of 0.0029. The data for *n*–octane may be slightly affected by impurities in the sample investigated. However, the $\frac{dt}{dp}$ ratio is not very sensitive to small amounts of contaminating substances, especially when of a nature similar to the main substance.

With the introduction of the method of comparative measurements into ebulliometry, the accuracy of determination of $\frac{dt}{dp}$ ratio is high enough to consider this constant as a fundamental one for characterizing liquid substances.

The author tenders his thanks to B. J. Mair and F. W. Rose, Jr., for furnishing the substances used in this work. He also expresses his gratitude to the Polish Fundusz Kultury Narodowej w Warszawie (Polish Fund of National Culture in Warsaw) for financial aid.

WASHINGTON, July 1, 1936.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP922

Part of Journal of Research of the National Bureau of Standards, Volume 17, September 1936

BOILING POINT OF ETHYL ETHER AND ITS RELATION TO PRESSURE

By Mieczysław Wojciechowski [1]

ABSTRACT

Ethyl ether of a high degree of purity was prepared, and its boiling point was found to be 34.481 ± 0.003° C. The $\frac{dt}{dp}$ ratio of ethyl ether (degrees per mm at 760 mm of Hg) is 0.0372.

Many attempts have been made to determine the exact boiling point of ethyl ether. The large discrepancies in the results reported are on the one hand due to difficulties connected with the purification of this important substance and on the other hand to a lack of ebulliometric technic adequate to insure high precision of the determination of the boiling point and $\frac{dt}{dp}$ ratio.

The impurities in ethyl ether are partly the products of side reactions in its manufacture, and are partly connected with its chemical nature, as it tends to decompose somewhat, especially when exposed to light or when heated with drying agents. The most persistent impurity is water. A mixture of ethyl alcohol and ether shows very marked positive deviations from Raoult's law, especially for small concentrations of ethanol. This indicates that it is difficult to prepare ether free from alcohol by distillation, even in an efficient column, and therefore the ethanol should be carefully washed out with water.

According to the nomenclature of Swietoslawski,[2] water forms with ether a homoazeotropic-heterozeotropic system, the boiling points of which are slightly below that of ether. For this reason small amounts of water in ether to be used for the determination of its boiling point and related properties are best removed by digestion with phosphorus pentoxide in the pot of an efficient still, after which the ether should be distilled directly into the ebulliometer to avoid any contact with moist air. For this purpose an efficient 40-bulb Swietoslawski [3] distilling column was used in this work. To control the purity of the substance under investigation, Swietoslawski's sensitive ebulliometric test of purity was used. In principle it is based on the measurement of the difference, Δt, between the boiling point and condensation temperature in an ebulliometer of standardized dimensions.[4] The

[1] Guest worker from Polytechnic Institute, Warsaw, Poland.
[2] W. Swietoslawski, Bul. Int. Acad. Polonaise [A] 1934, 472.
[3] W. Swietoslawski, J. chim. phys. 27, 329 (1930); Bul. Soc. Chim. France [4] 49, 1563 (1931).
[4] W. Swietoslawski, Bul. Int. Acad. Polonaise [A] 1929, 434; Bul. Soc. Chim. France 49, 1563 (1931); Z. phys. Chem. [A] 160, 259 (1932).

purer the substance is the smaller will be Δt, and for an absolutely pure substance or an azeotropic mixture, the boiling point and temperature of condensation are equal, thus giving Δt equal to zero.

For determining the boiling point and $\frac{dt}{dp}$ ratio of ether, Swietoslawski's ebulliometric technic [5] and the comparative method of measurements with water as a reference liquid were used. The measurements of temperature were made with a potential terminal, strain-free platinum resistance thermometer [6] having a coiled filament, and calibrated in the Heat Division of the National Bureau of Standards. The normal boiling point was calculated by the use of a formula previously reported,[7] in which t_s represents the normal boiling point

$$t_s = t'_s + \frac{dt_s}{dt_w}(100 - t'_w)$$

of the substance under investigation, t'_s the boiling point of the substance actually measured, t'_w the boiling point of water actually measured under the same pressure as t'_s, and $\frac{dt_s}{dt_w}$ the ratio of the coefficients $\frac{dt}{dp}$ for the given substance and water.

The ratio $\frac{dt}{dp}$ for the substance under investigation was calculated from the data on $\frac{dt_s}{dt_w}$ by multiplying the latter by the $\frac{dt}{dp}$ ratio of water at the same pressure.

$$\left(\frac{dt}{dp}\right)_s = \frac{dt_s}{dt_w}\left(\frac{dt}{dp}\right)_w$$

In these measurements, pressure is defined by the boiling point of water.

Two kilograms of nearly anhydrous ether, kindly furnished by the Mallinckrodt Chemical Works, through the courtesy of H. V. Farr, for a related investigation on the determination of water in ether, was boiled for 12 hours over phosphorus pentoxide in the 40-bulb distilling column under total reflux, and then slowly distilled, the first 400 ml of distillate being removed. Then a 50-ml sample was distilled directly into the ebulliometer, and its ebullioscopic properties determined at once. The difference, Δt, between the boiling point and condensation temperature of this sample was 0.001° C. The substance therefore was of the fifth or highest degree of purity on Swietoslawski's scale.[8] The measurement of Δt was repeated after the determination of the boiling point. No change in the purity of the substance was detected.

The ratio $\frac{dt_s}{dt_w}$ was measured for the pressures corresponding to

[5] W. Swietoslawski, Ebuljometrja, Warszawa (1935); J. chim. phys. **27**, 496 (1930); Roczniki Chem. **9**, 266 (1929).
[6] C. H. Meyers, BS J. Research **9**, 807 (1932) RP508.
[7] M. Wojciechowski, BS J. Research **17**, 453 (1936) RP921.
[8] W. Swietoslawski, IX Congreso Int. Quim. Pura Aplicada, Madrid, 1934, 13.

those of water when boiling at 100.962° C and 97.749° C, and this ratio for any pressure included in these limits may be calculated by interpolation. The numerical data on the dt_s/dt_w ratio are presented below.

$\frac{dt_s}{dt_w}$	Boiling point of water
1. 0063	100. 962
1. 0067	97. 74

The normal boiling point of ether was found to be 34.48_1° C, and $\frac{dt}{dp}$ at 760 mm, calculated from the above data, equals 0.0372, taking $\frac{dt}{dp}$ of water as 0.0370.

Table 1 contains a comparison of the results obtained by the author with values previously reported in the literature.

TABLE 1.—*Comparison of the results with the data of previous observers*

Author	Boiling point	$\frac{dt}{dp}$
	°C	°C/mm
E. Beckmann and P. Fuchs [1]	34. 6	0. 0398
H. H. Perkin [2]	34. 60	. 37 (10 mm)
S. Young [3]	34. 6	. 37 (10 mm)
J. Wade and H. Finnemore [4]	34. 5	
B. H. Carroll, G. K. Rollefson, and J. H. Mathews [5]	34. 0	
J. Timmermans and F. Martin [6]	34. 60	. 036
J. H. Mathews [7]	34. 66	
Calculated from temperature vapor pressure curve reported by E. A. Louder, T. R. Briggs, and A. W. Browne [8]	34. 45	
Author	34. 481 + 0. 003	. 0372

[1] Z. phys. Chem. **18**, 495 (1895).
[2] J. Chem. Soc. **45**, 430 (1894).
[3] Distillation, Dublin, 1903; J. Chem. Soc. **85**, 935 (1904).
[4] J. Chem. Soc. **95**, 1840 (1909).
[5] J. Am. Chem. Soc. **47**, 1785 (1925).
[6] J. chim. phys. **23**, 411 (1926).
[7] J. Am. Chem. Soc. **48**, 569 (1926).
[8] Ind. Eng. Chem. **16**, 932 (1929).

The purity of the ether used in this investigation, as indicated by the value of 0.001° for Δt, was such that the accuracy of the boiling point can hardly be in question by more than 0.003°, allowing 0.001° for possible error caused by the use of the method of comparative measurements.

The author expresses his gratitude to F. W. Schwab and H. Matheson for their assistance in the purification of the substance. Further, the author expresses his gratitude to the Polish Fundusz Kultury Narodowej w Warszawie (Polish Fund of National Culture in Warsaw) for financial aid.

WASHINGTON, July 10, 1936.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP923

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YOUNG'S MODULUS OF ELASTICITY, STRENGTH, AND EXTENSIBILITY OF REFRACTORIES IN TENSION

By R. A. Heindl and L. E. Mong

ABSTRACT

Young's modulus of elasticity, strength, and extensibility were determined at ordinary temperatures upon the following materials in tension: 16 brands of fire-clay brick with a wide range in silica content, representing the stiff-mud, dry-press, and handmade methods of forming; one brand each of silica brick, chrome, forsterite, 60 percent alumina, 80 percent alumina, and of mullite. A comparison is made of the tensile properties of specimens obtained parallel to the 9-in. dimension with those obtained parallel to the 4½ in. dimension. The effects of method of setting the bricks in the kiln during firing, load during firing, and weight of the brick on the tensile properties of fire-clay brick made by the dry-press process were briefly studied. With one exception, the tendency is quite general for the tensile properties to vary greatly not only between units but also within the unit.

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I. INTRODUCTION

The brittleness of refractory products has in the past been a serious handicap to the study of their tensile properties. Within recent years the development of the optical strain gage for measuring minute length changes has given the research worker a tool which has eliminated most of the difficulties encountered in such a study, so that strain measurements of all types of refractory materials can now be made with reasonable accuracy.

Although refractories are ordinarily subjected to comparatively small external loads, more information on their little-known structural properties may lead to a better understanding of their behavior in certain types of service. A knowledge of the tensile properties of fired refractory products is desirable because of the trend toward fairly large shapes in hanging roofs designed for modern high-power boiler settings, heat treating and other furnaces. Also, there is often a decided lack of agreement in the results of certain tests of apparently duplicate samples of refractory bricks.

A study was therefore undertaken to make information available on the tensile properties of the standard 9-inch-size firebrick and also to determine the extent of the variation in these properties within the brick and between bricks. This shape is produced in largest quantities, is readily obtainable, enables a selection representative of the different localities and processes of manufacture, different degrees of heating, and different methods of setting in the kiln. The specimens used for study were machined from sections, the axes of which were initially lengthwise or crosswise to the brick. Measurements were made of the ultimate stress, Young's modulus and maximum strain or extensibility of the specimens tested in tension at room temperature.

II. MATERIALS

Sixteen brands of fire-clay bricks, and one brand each of silica, chrome, forsterite, 60 percent alumina, 80 percent alumina, and a specially prepared shape of mullite (cylinders 9½ in. long and 2½ in. in diam) were obtained from 10 manufacturers in different locations in the United States. Seven of the 16 brands of fire-clay bricks were formed by the dry-press, 5 by the stiff-mud, and 4 by the handmade process.

1. CHEMICAL ANALYSES [1]

The chemical compositions of the fire-clay bricks are given in table 1. The method of analysis followed was, in general, that described by Lundell and Hoffman [2] for refractories.

The compositions show the wide range in silica, alumina, and flux contents of the materials. The silica ranges from 14.9 percent in the high-alumina brick to 96 percent in the silica brick. In the fire-clay brick the silica ranges from 47.8 to 80.7 percent. The flux ranges from 3.2 to 7.8 percent.

[1] Made by E. H. Hamilton of the Bureau staff.
[2] *Analysis of bauxite and of refractories of high alumina content.* BS J. Research, 1, 91 (1928) RP5.

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TABLE 1.—*Tensile and other properties of firebrick* [a]

Brand [b]	Method of manufacture [c]	Pce	Porosity	Chemical composition					Young's modulus of elasticity			Strength			Extensibility			
				SiO_2	Al_2O_3	Total flux	$Fe_2O_3+TiO_2$	P_2O_5	Lengthwise	Crosswise	All specimens	Lengthwise	Crosswise	All specimens	Length wise	Cross-wise	All specimens	Coefficient of variation [f]
		Cone	%	%	%	%	%	%	1,000 lb/in.²	1,000 lb/in.²	1,000 lb/in.²	lb/in.²	lb/in.²	lb/in.²	%	%	%	%
1	DP	34	16.2	47.8	44.4	7.8	3.1	1.06	1,885	2,200	1,990	385	290	355	0.0205	0.0135	0.0185	4.2
2	DP	33-34	21.1	53.9	40.2	5.9	3.7	.11	1,190	1,285	1,225	275	240	265	.0230	.0190	.0225	26.0
2 [d]	DP								960	1,145	1,025	245	185	225	.0255	.0165	.0225	10.2
3L [e]	DP	33	17.8	51.5	41.2	7.3	4.2	.08	1,530	2,530	1,860	355	350	355	.0235	.0140	.0200	2.9
3H [e]	DP	33	17.6	51.6	40.7	7.7	4.5	.09	2,160	3,400	2,575	430	465	440	.0200	.0135	.0180	11.2
4	HM	33	25.8	50.8	42.7	6.7	4.4	.18	545	670	585	125	90	115	.0240	.0140	.0205	31.0
5	DP	32-33	20.7	50.9	42.0	7.2	4.7	.16	735	1,120	865	180	195	185	.0250	.0185	.0230	18.0
6	SM	32-33	21.5	52.0	41.2	6.8	4.4	.18	1,465	1,655	1,525	335	235	305	.0230	.0150	.0205	12.9
6 [d]	SM								1,685	1,950	1,775	360	335	350	.0215	.0170	.0200	10.5
7	HM	32	25.1	58.5	34.8	6.7	4.1	.09	1,415	1,545	1,460	325	265	305	.0235	.0170	.0210	2.2
7 [d]									1,735	1,450	1,640	335	235	300	.0195	.0165	.0185	25.5
8	SM	31	21.8	56.2	37.0	6.8	4.3	.09	1,560	1,515	1,545	365	325	350	.0235	.0220	.0230	11.7
8 [d]									1,265	1,170	1,235	305	260	290	.0245	.0220	.0235	16.9
9	DP	33	23.3	54.2	39.5	6.4	4.5	.11	1,960	2,320	2,080	430	385	415	.0220	.0170	.0205	8.7
10	SM	32-33	22.9	53.5	40.2	6.4	4.6	.10	3,865	2,465	3,400	555	415	510	.0145	.0170	.0155	9.6
11	DP	32-33	18.7	56.9	37.8	5.3	2.5	.52	595	525	575	165	150	160	.0275	.0285	.0280	20.0
12	SM	32-33	8.9	59.0	36.5	4.6	2.9	.13	5,500	4,760	5,255	755	370	630	.0140	.0090	.0120	50.2
13	HM	32-33	22.0	59.1	36.0	4.9	3.0	.12	2,440	2,500	2,460	405	490	435	.0165	.0200	.0175	11.5
14	DP	31-32	23.2	58.1	34.5	7.4	4.9	.11	1,855	2,205	1,970	375	395	385	.0205	.0185	.0200	15.2
15	SM	31-32	25.4	65.3	29.4	5.3	3.5	.08	2,130	1,875	2,045	470	230	390	.0220	.0130	.0190	11.7
15 [d]	SM								2,135	1,510	1,925	425	295	370	.0205	.0195	.0200	8.5
16	HM	29-30	29.9	80.7	16.1	3.2	2.4	.07	490	565	515	175	180	180	.0365	.0330	.0355	19.4
17	HM	32-33	29.3	96.0					470	505	485	200	275	225	.0420	.0550	.0465	14.8
18	DP	35	19.8	36.8	55.7	7.4	3.8	.36	3,235	3,405	3,300	660	560	620	.0205	.0165	.0190	33.0
19	DP		26.8	14.9	79.3	5.7	4.1	.39	4,680	5,475	4,950	1,055	895	1,005	.0225	.0165	.0205	4.6
20			26.6						3,025	4,190	3,415	555	565	555	.0185	.0140	.0170	9.4
21	DP		24.3						1,000	1,050	1,015	235	225	230	.0235	.0215	.0230	7.4

[a] Values of tensile properties represent average values for 3 bricks.
[b] Brands 1 to 16 are fire-clay brick, 18 and 19 high-alumina, and 17, 20, and 21 are silica, chrome, and forsterite, respectively. Information on the mullite refractory is given in table 3.
[c] DP, dry press; HM, handmade; SM, stiff-mud.
[d] Represent duplicate samples.
[e] 3L and 3H same brand of brick, but fired at cones 12 and 14, respectively.
[f] The two lengthwise specimens from each brick were taken as the unit for the sample.

2. PYROMETRIC-CONE EQUIVALENTS

The pyrometric-cone equivalents (pce or softening points) were determined according to the ASTM standard method, serial designation C 24–33.[3] The values, given in table 1, ranged from 29–30 to 35. None of the pce values of the so-called special type of refractories are included except that of the 60 percent of alumina brick.

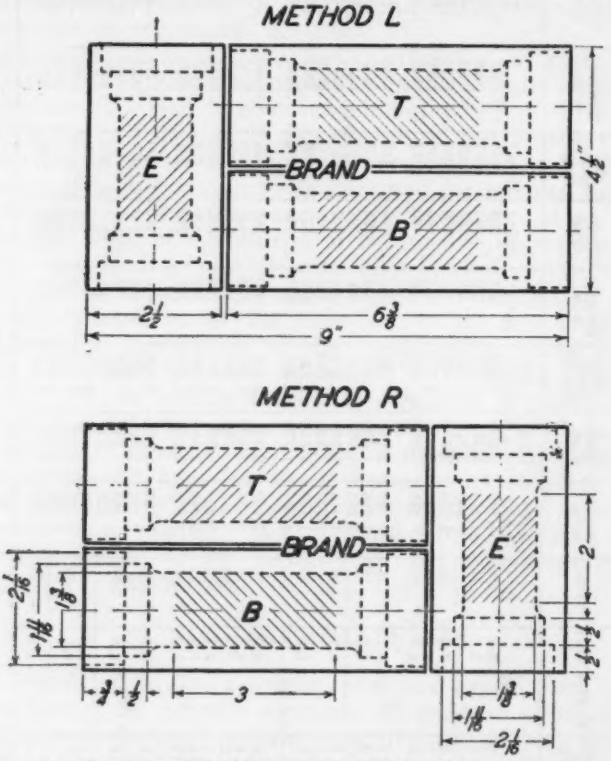

FIGURE 1.—*Sections of the brick from which specimens were prepared*

In each sample of three bricks two were cut by method L and one by method R.

3. POROSITY

The porosity determinations were made as follows: three cylindrical specimens,[4] approximately 2¾ in. long and 1⅜ in. in diam, prepared from three different bricks of each brand, were saturated by boiling in water for 1½ hr under a pressure of 4 mm of mercury. The specimens remained under water and under pressure which gradually increased to atmospheric overnight. They were then weighed. The porosity, recorded in percent, is the ratio of the volume of water absorbed to the bulk volume of the specimen. The porosities (table 1) range from 8.9 percent for a stiff-mud fire-clay brick to 29.9 percent for a highly siliceous fire-clay brick.

The chemical analysis, pyrometric-cone equivalent, and porosity are given merely for descriptive purposes and no attempt is made to correlate these properties with the tensile properties.

[3] American Society for Testing Materials Book of Standards for 1933, pt. 2, p. 184.

[4] Cut from ruptured tensile-test specimens.

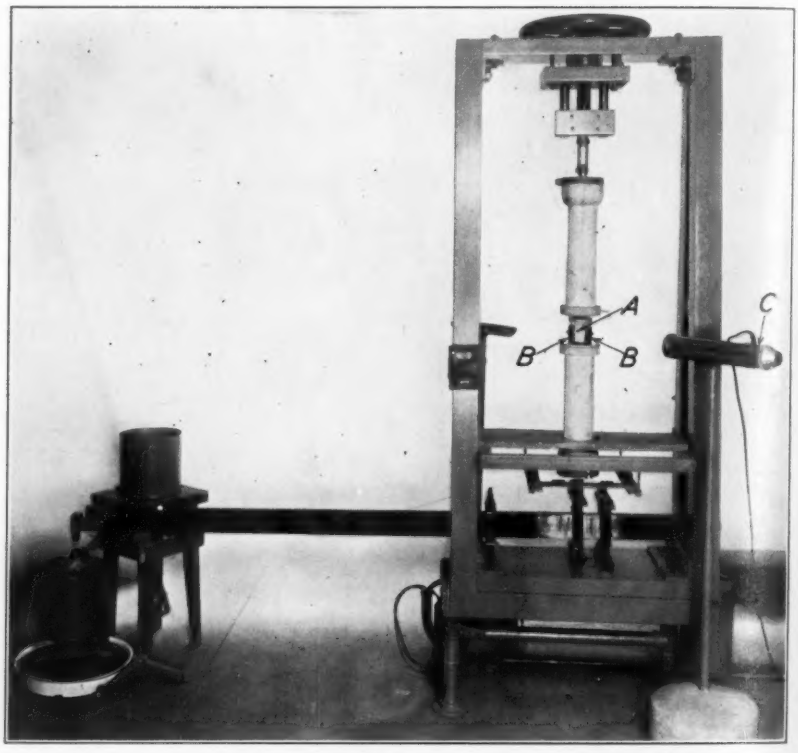

FIGURE 2.—*Apparatus for obtaining tensile properties of refractory materials.*

Specimen *A*, with strain gages *B* attached, and the autocollimator *C* are all in position for making observations.

U. OF MICH.

III. SPECIMENS AND APPARATUS

1. SPECIMENS

Cylindrical test specimens with shoulders and flanges, as shown in figure 1, were ground to size on a small lathe from sections cut from individual bricks. The crosswise specimen (marked E) could be taken from the end to the left or to the right of the brand name.

2. DESCRIPTION OF APPARATUS

Figure 2 shows the testing machine for making the tensile tests with the optical strain gage of the Tuckerman type[5] attached to a specimen and the autocollimator in position for an observation. The testing machine is of the counterbalanced simple beam type with the fulcrums spaced to give a 20:1 ratio at the straining clevis. Fulcrum plates of the A. H. Emery type are provided in place of knife edges to insure constancy of the lever ratio. The load is obtained by means of no. 12 lead shot flowing into a container at one end of the beam at a rate to cause a load increase of 290 lb/min. The flow of shot is controlled by means of valves actuated by solenoids.

Figure 3 shows the assembly of the specimen and strain gages, upper and lower specimen holders or grips[6] and aligning bearings. All bearing surfaces of grips and specimens are ground parallel to insure their proper alignment. The two strain gages are mounted diametrically opposite as indicated. To avoid shifting of the lozenge on the irregular

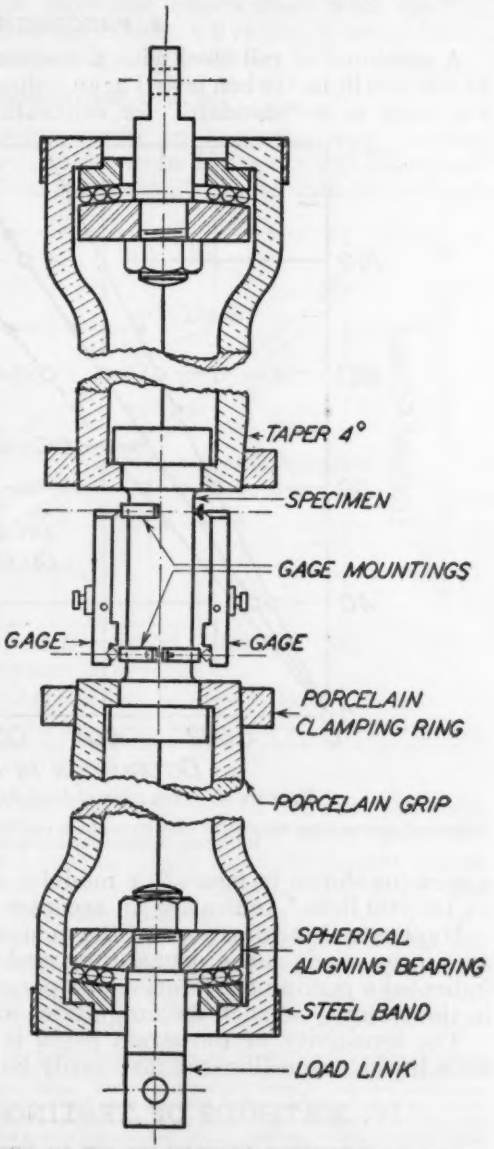

FIGURE 3.—*Assembly of the specimen, strain gages, gage mountings, porcelain specimen grips, and aligning bearings.*

[5] *Optical strain gages and extensometers.* Proc. Am. Soc. Testing Materials **23**, pt. II, p. 602 (1923).
[6] Porcelain holders or grips were made and used because plans have been made to study tensile properties of refractories at elevated temperatures.

surface of the specimen as well as to avoid injuring the knife edge and lozenge of the gages by abrasive contact with the specimen, they are rested on metallic rings attached to the specimen. Each ring or gage mounting contacts the specimen at four points approximately equally spaced around the circumference. Tests with and without rings indicated that the rings did not affect the results.

3. PRECISION

A specimen of rail steel with a modulus of elasticity in tension of 31,800,000 lb/in.^{2} (when tested in an ordinary type of testing machine), was used as a "standard" for calibrating the machine. With the

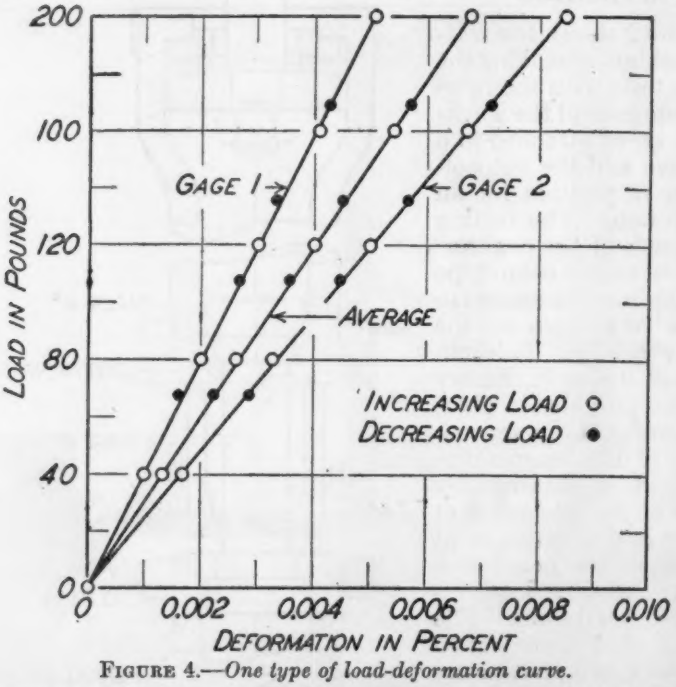

FIGURE 4.—*One type of load-deformation curve.*

Individual gage readings are shown. The stress-strain relation obtained during loading of the specimen is the same as that obtained during unloading.

apparatus shown in figure 2, a modulus of elasticity was obtained of 32,100,000 lb/in.^{2}, indicating an accuracy of about 1 percent.

Duplicate determinations of the modulus of elasticity of refractory specimens made after dismantling and reassembling of the setup indicated a maximum variation of 3 percent. However, the variation in the majority of such determinations was less than 2 percent.

The sensitivity of the strain gages is 0.000002 in., to which the scale in the autocollimator may easily be read.

IV. METHODS OF TESTING AND SAMPLING

1. YOUNG'S MODULUS OF ELASTICITY IN TENSION

(a) LENGTHS AND POSITIONS OF STRAIN GAGES

After the specimen was placed in the holders preparatory to testing, two strain gages of the desired length were attached. The gage length was 2 in., but extensions were provided to accommodate specimen

gage lengths of 3 and 6 in. Two gages were used in order to obtain an average deformation. Inasmuch as the center of a brick is usually softer than the outside, some differences could be expected in deformation readings obtained by the two gages. No readings were taken for at least 15 min after placement because of the sensitiveness of the gages to body temperature. Observations were made to determine if the gages had become stabilized before loads were applied. The strain was increased in the specimens in five nearly equal increments up to a total of approximately 0.01 percent.

(b) STRESS-STRAIN CURVES

One type of load-deformation curve for a specimen of fire-clay brick, using a 3-in. gage length, is shown in figure 4. The individual values obtained with each of the two gages, together with the average

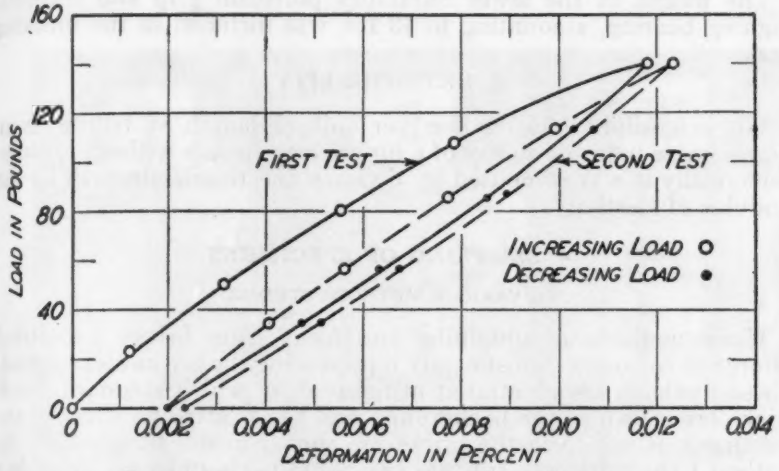

FIGURE 5.—*A second type of load-deformation curve.*

The mean reading of the two gages is shown. The stress-strain relation during unloading of the specimen is not the same as that obtained during loading. A permanent set of the specimen is indicated after each of the two tests.

values, are shown. In this case the variation in deformation indicated by the two gages, based on the average values, was 50 percent.[7] This type of curve illustrates a case in which the deformation values obtained with decreasing loads are, within experimental error, the same as those obtained with increasing loads.

Figure 5 shows a second type of load-deformation curve where the deformation values obtained with decreasing loads are not the same as those obtained with increasing loads and indicate that there was permanent elongation of the specimen. The value of each point is

[7] The deformations of six specimens from two bricks were obtained by placing the two available strain gages successively at four pairs of different positions of approximately equal spacing around each specimen using individual protective mountings for the gages. This was done to determine how uniformly any two positions of the gages diametrically opposite would yield the same average deformation as any other two diametrically opposite gages. The maximum variation based on the average deformation ranged from 1.5 to 5 percent for 20 pairs of values (4 pairs for each of 5 specimens) and 11.7 percent for the 4 pairs of readings for the sixth specimen. Some of the variation may be accounted for by the change in modulus of elasticity of the material between loadings. The extreme variation of 11.7 percent is so far out of line from the other 23 values that it seems probable it is in error.

If the extreme individual values for the specimen which showed the greatest differences are considered without regard to whether or not gages were diametrically opposite, the greatest variation based on the average was 72 percent and the specimen which showed the least difference for all eight readings showed a variation of 13.5 percent.

the average reading of the two gages. The modulus of elasticity was computed from the line resulting from the average of the load-deformation curves obtained during a second test, also shown in figure 5 (average line not shown) by the usual stress-strain formula, namely:

$$\text{Young's modulus} = \frac{\text{stress}}{\text{strain}} = \frac{\text{load}}{\text{deformation per unit of length X area}}.$$

2. TENSILE STRENGTH

The same specimens on which the elasticity had been determined were in general used for tensile-strength determinations. After the elasticity measurements had been obtained, the strain gages were removed and the flow of shot continued until the specimen ruptured.

The weight of the lower refractory porcelain grip and spherical aligning bearing, amounting to 13 lbs, was included in the breaking load.

3. EXTENSIBILITY

The extensibility (elongation per unit of length at failure) is an approximate index of ability of a firebrick to stretch without rupture; numerically it was computed by dividing the tensile strength by the modulus of elasticity.

4. SAMPLING OF SPECIMENS

(a) VARIOUS METHODS STUDIED

Three methods of obtaining specimens from bricks were tried before one considered most nearly representing the bricks was adopted. These methods are illustrated in figure 6, in which standard 9-inch bricks are shown in the background and the relative positions of the specimens as cut from the bricks are shown in the foreground. In method I the brick was cut into two equal parts (9 by 2¼ by 2½ in.) parallel to the 9 in. dimension, one part (F) was prepared to accommodate a 6-in. gage length and the other (G) to accommodate a 2-in. gage length in the central portion of the specimen and a specimen on either end (A, H) for tensile-strength tests only. In method II the brick was cut into four equal portions (M, L, K, and J) parallel to the 4½-in. dimension and finished to accommodate 2-in. gage lengths. In method III the two specimens (T, B) with an over-all length of 6⅞ in. were prepared from portions of the brick cut parallel to the 9 in. dimension and one specimen (E) from a section cut parallel to the 4½ in. dimension.

Results of tests of specimens prepared by the three different methods of sampling are given in table 2. The first three groups of specimens are from bricks made by manufacturer X by three different processes. The comparisons of tensile properties between bricks are of uncertain value because one brick only was sampled by each method. However, the three methods of specimen sampling illustrate effectively the impossibility of cutting a simple specimen from any one portion of the brick which can be considered as representative. For example, in the first group of bricks, manufactured by the handmade process, the modulus of elasticity of specimen G was 59 percent greater than that of F and the tensile strength was about 120 percent greater.

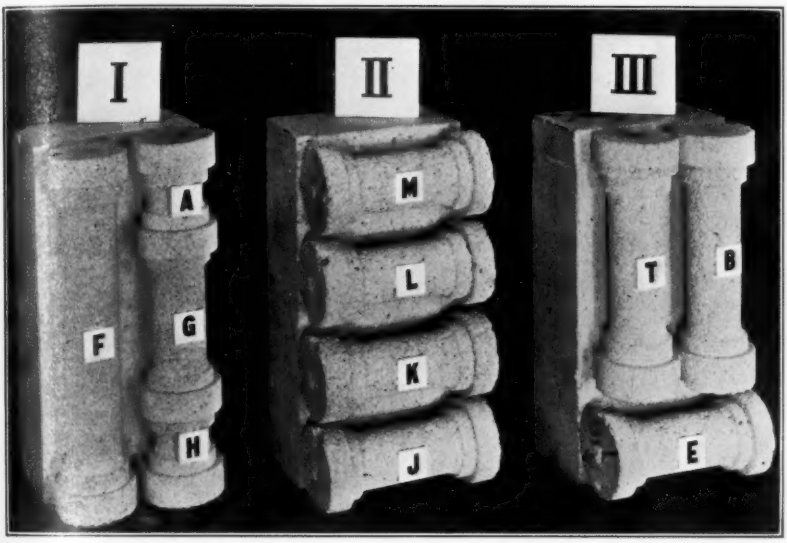

FIGURE 6.—*Different types of test specimens and the methods by which they were laid out.*

Method III was adopted because it was considered the specimens were more nearly representative of the brick.

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The tensile-strength determinations of specimens A, G, and H serve to illustrate the variability along the longitudinal half of the brick. In the case of the four lateral specimens, illustrated by method II, the highest value of the modulus of elasticity (brick 2, table 2) is about 40 percent above that of the lowest value. Both the elasticity and strength of this brick indicate considerable difference in structure between one end of the brick and the other. The average value for the specimens from brick 1 and that for brick 2 indicate the probability of some difference in their treatment during manufacture. The specimens in brick 3 combined methods of sampling I and II, as shown in figure 6, III. In this case the mean Young's modulus of the two lengthwise specimens was about 50 percent greater than that of the crosswise specimen. The two lengthwise specimens are in excellent agreement. Considering the nine specimens of all three bricks the mean elasticity value for the four specimens sampled lengthwise was in good agreement with the mean of the five specimens sampled crosswise.

TABLE 2.—*Tensile properties of fire-clay brick sampled by different methods*

Manufacturer	Method of manufacture	Brick no.	Specimen [1]	Modulus of elasticity	Strength	Extensibility	Maximum [2] extensibility variation in each brick
				1,000 lb/in.²	lb/in.²	%	%
		1	F	1,410	180	0.0130	32.2
			G	2,240	405	.0180	
			H	----------	370	----------	----------
			A	----------	255	----------	----------
		2	J	2,380	295	.0125	17.0
			K	2,760	340	.0125	
X	Handmade		L	3,300	350	.0105	
			M	3,270	410	.0125	
		3	T	3,500	620	.0175	2.8
			B	3,430	625	.0180	
			E	2,200	440	.0200	----------
			Lengthwise avg	2,645	460	.0165	----------
			Crosswise avg	2,780	365	.0135	----------
		4	F	1,305	385	.0295	26.9
			G	1,625	365	.0225	
			H	----------	435	----------	----------
			A	----------	480	----------	----------
		5	J	1,260	280	.0225	30.1
			K	1,495	300	.0200	
X	Dry Press		L	1,990	330	.0165	
			M	1,725	350	.0205	
		6	T	1,330	390	.0295	20.6
			B	1,600	380	.0240	
			E	930	255	.0275	----------
			Lengthwise avg	1,465	380	.0265	----------
			Crosswise avg	1,480	305	.0215	----------
		7	F	3,110	540	.0175	22.9
			G	3,620	800	.0220	
			H	----------	495	----------	----------
X	Stiff mud		A	----------	660	----------	----------
		8	J	2,010	370	.0185	13.0
			K	----------	----------	----------	
			L	395	85	.0210	
			M	2,710	505	.0185	

[1] Key letter of specimen corresponds to that shown in figure 6.
[2] Specimen E not included in determining the spread.

TABLE 2.—*Tensile properties of fire-clay brick sampled by different methods*—Con.

Manufacturer	Method of manufacture	Brick no.	Specimen	Modulus of elasticity	Strength	Extensibility	Maximum extensibility variation in each brick
				1,000 lb./in.	lb./in.²	%	%
X	Stiff mud	9	T	3,220	325	.0100	10.5
			B	3,630	650	.0180	
			E	2,690	350	.0130	
			Lengthwise avg	3,395	580	.0170	
			Crosswise avg	1,950	320	.0180	
Y	Dry press	10	F	1,120	160	.0140	42.3
			G	1,380	295	.0215	
			H		410		
			A		385		
		11	J	5,100	435	.0085	32.3
			K	4,720	335	.0070	
			L	4,150	365	.0090	
			M	5,450	355	.0065	
		12	T	2,610	505	.0195	13.4
			B	2,960	500	.0170	
			E	3,760	340	.0090	
			Lengthwise avg	2,035	365	.0180	
			Crosswise avg	4,635	365	.0080	
Z	Dry press	13	F	320	75	.0230	23.1
			G	380	110	.0290	
			H		95		
			A		100		
		14	J	880	125	.0140	43.0
			K	1,030	125	.0120	
			L	1,060	190	.0180	
			M	905	190	.0210	
			Lengthwise avg	350	90	.0260	
			Crosswise avg	970	155	.0160	

Specimens from bricks 4, 5, and 6, made by the dry-press process, do not show a variation in values between bricks as great as was shown in bricks 1, 2, and 3. The variation within an individual brick was about the same in magnitude as in bricks 1, 2, and 3 of the first group. The mean modulus values for the specimens cut lengthwise to the brick are approximately equal to the mean values of those cut crosswise.

Specimens cut from bricks 7, 8, and 9, manufactured by the stiff-mud process, showed greater variations between bricks. Variation in values was especially evident in specimens sampled in accordance with method II, figure 6. The two specimens from the central portion of the brick were unsatisfactory because of laminations. As indicated in the table, K broke before any data were obtained and specimen L had unusually low tensile properties caused by laminations.

There is an unusually wide range in tensile properties between bricks 10, 11, and 12, made by manufacturer Y by the dry-press method, due possibly to differences in kiln temperature during manufacture. On the other hand, variations in the modulus of elasticity within the brick are not as wide as in some of the other brands.

Specimens from bricks 13 and 14, also of the dry-press variety but made by manufacturer Z, gave the lowest tensile strength and modulus of elasticity of those recorded in this table. Variation between bricks

was again high, but the values obtained with test specimens cut in the same manner were quite uniform.

The range in extensibility of all specimens recorded in table 2 is from 0.0065 percent to 0.0295 percent. The greatest range (0.0065 to 0.0215 percent) in any one group is represented by bricks 10, 11, and 12. These data illustrate the very wide range existing in this important property between bricks made by different manufacturers, bricks made by the same manufacturer but by different processes, and bricks made by any one manufacturer and one process of manufacture.

(b) VARIATION IN MODULUS OF ELASTICITY OVER 6-INCH GAGE LENGTHS

Four specimens from three brands of bricks and three specimens of a mullite refractory were prepared to accommodate 6-in. gage lengths (see specimen F, fig. 6). Table 3 gives Young's modulus in tension for the three 2-in. gage lengths making up the 6-in. gage length. In addition, Young's modulus and tensile strength are given for the 6-in. gage length of the specimens. These data illustrate the variability in tensile properties of bricks which may exist along the longitudinal axis and that the modulus of elasticity taken over the 6-in. length is very nearly the same as the mean of the three 2-in. gage lengths.

TABLE 3.—*Young's modulus of elasticity of firebrick in tension*

[Comparison of 2-in. and 6-in. gage lengths of the same specimen]

Manufacturer [a]	Method of manufacture	Modulus of elasticity				Strength [c]
		2-in. gage length			6-in. gage length	
		Bottom	Middle	Top		
		1,000 lb/in.²	1,000 lb/in.²	1,000 lb/in.²	1,000 lb/in.²	lb/in.²
X	Dry-press	1,210	1,340	1,410	1,305	385
X	Stiff-mud	3,670	3,230	2,560	3,110	540
X	do	2,560	3,490	3,490	3,050	460
Z	Dry-press	295	390	380	320	75
W [b]		6,720	6,350	6,950	6,720	665
W		6,700	6,950	7,050	6,950	1,115
W		6,220	6,570	6,570	6,330	855

[a] X and Z, fire-clay brick: W, mullite refractory.
[b] Samples submitted were cylinders 9½ in. long and 2½ in. in diameter.
[c] Determined after modulus of elasticity data for 6-in. specimen had been obtained.

(c) VARIATION IN MODULUS OF ELASTICITY WITH CHANGE IN CROSS SECTION OF SPECIMEN

A few tests were made to determine the effect on the modulus of elasticity of changing the diameter of the specimen. For this purpose three brands of bricks were used, the specimens in two cases were prepared to accommodate 6-in. gage lengths and one for a 3-in. gage length. In the former case the specimens were tested with three different cross-sectional areas, of approximately 1.75, 1.50, and 1.10 in.², respectively, and in the latter with cross-sectional areas of 1.50 and 1.10 in.², respectively. The Young's moduli of these specimens were measured in tension without rupturing the specimens in order to permit retesting. After the first test these specimens were machined to the next smaller size and again tested and the same procedure followed for the third test for specimens of brands 2 and 8.

The results are given in table 4. The spread between the maximum and minimum values for the different cross-sectional areas was considered reasonable.

TABLE 4.—*Young's modulus of elasticity of firebrick in tension*

[Comparison of values for specimens of different cross sections]

Brand	Method of manufacture	Gage length	Cross-sectional area	Modulus of elasticity	Spread
		in.	in.²	1,000 lb/in.²	%
2	Dry-press	6	1.77 1.50 1.12	1,250 1,255 1,260	0.8
8	Stiff-mud, repress	6	1.75 1.49 1.12	1,220 1,180 1,145	6.3
12	Stiff-mud	3	1.49 1.11	7,080 7,100	.3

(d) METHOD OF SAMPLING SPECIMENS ADOPTED

The method of sampling designated III (fig. 6) was adopted because it would give a measure of the tensile properties of specimens prepared from sections cut crosswise and lengthwise to the brick. The over-all length of specimens was either 4½ or 6⅜ in., suitable for 2-in. and 3-in. gage lengths, respectively. The diameter of the flanges was 2 1/16 in. and that of the cylinder 1⅜ in., the latter with a cross-sectional area of about 1.50 in.²

The final tests were made on nine specimens from three bricks; in two bricks the crosswise specimens were cut from the end to the left of the brand name (method L) and in the third brick from the end to the right of the brand name (method R), figure 1. It is possible that the top and bottom faces during forming and repressing are not always in the same relative order with respect to brand name. This applies especially to bricks formed by the handmade process, where the brick is stamped during repressing.

For the purpose of this investigation the cross-sectional area of about 1.50 in.² was adopted for the test specimens. This was, on the one hand, small enough to avoid breaking the grips and to secure flanges as large as possible for good seating of the specimens in the grips, and on the other hand, was as large as possible in order to obtain a representative volume of material within the gage length.

V. RESULTS AND DISCUSSION

1. COMPARISON OF TENSILE PROPERTIES WITHIN THE BRICK, BETWEEN BRICKS, AND BETWEEN BRANDS

Process of forming, temperature of firing during manufacture, method of kiln setting, particle size, and composition affect the properties. With the exception of particle size, some discussion will follow relative to the apparent effects of each of these variables on the tensile properties. Data were obtained in only one case (brand 3) on the influence of firing temperature on the tensile properties, but that example shows that firing temperature is an important factor in the magnitude of the variation of the tensile properties.

Table 1 gives the average modulus of elasticity, tensile strength and extensibility of 3 bricks taken from each of 21 brands. The columns headed "lengthwise" give values from data obtained on six specimens and those headed "crosswise", values on three specimens. A third column headed "all specimens" gives the mean value of all nine specimens machined from the three bricks.

The group of three brands, 4, 5, and 6, represents one manufacturer's products, each formed by a different process. The group, brands 11, 12, and 13, represents a second manufacturer's products, each also formed by a different process. In the first group, stiff-mud brick had the highest modulus of elasticity and strength and the handmade, the lowest. However, the extensibility of the dry-press bricks (brand 5) exceeded appreciably that obtained on bricks made by the other two processes. This was true for specimens cut either lengthwise or crosswise. For brands 11, 12, and 13, the stiff-mud brick also had the highest modulus of elasticity and strength, but these properties were lowest for the dry-pressed bricks. The brick formed by the dry-press process (brand 11) also gave the greatest extensibility, much greater, in fact, than that of either brand 12 or 13. The extensibility of the crosswise specimen of brand 12 was exceptionally low, far lower than that of any other brand. In brands 9 and 10, a third manufacturer's products, the modulus of elasticity of the lengthwise specimens of the stiff-mud brick was about double that of the dry-press brick. However, the values of the crosswise specimens were not appreciably different in either modulus of elasticity or tensile strength. When the mean of all specimens is considered, the bricks made by the dry-press method were decidedly higher in extensibility than those made by the stiff-mud process. Brands 14, 15, and 15c, from another manufacturer, showed comparatively little difference in tensile properties regardless of method of manufacture; the only exception was shown by the crosswise specimen of the stiff-mud product. The combined average values for both samples of brand 7 and for both samples of brand 8, handmade and stiff-mud bricks of still another manufacturer, illustrate that a lower modulus of elasticity and higher strength may be obtained by the latter process of forming. The extensibility of the handmade (brand 7) is lower than that of the stiff-mud brick, although the reverse might be expected.[8]

Brand 16 is a highly siliceous fire-clay brick of low modulus of elasticity and low tensile strength. The ratio of strength to modulus of elasticity is high, resulting in high extensibility, a very favorable property in firebrick.

The change in tensile properties caused by a difference in firing temperature of approximately 80° C is illustrated by brand 3L (fired at cone 12) and 3H (fired at cone 14). Young's modulus and also the strength were decidedly greater for 3H than 3L, although the modulus increased much more than the strength and consequently resulted in a lower extensibility.

Brand 17, a silica brick (96 percent of silica), has a low modulus of elasticity and good strength, resulting in an unusually high extensibility for refractory brick. Brand 16, containing the next highest percentage of silica (80.6 percent), had the next highest extensibility,

[8] J. Am. Ceram. Soc. 16, 11 (1933). An adjustment of the particle sizes or of the composition might possibly overcome this condition.

much higher than that of the other brands (excepting the silica brick) tested. Brands 18 and 19 are high-alumina refractories. The modulus and strength of brand 18 are substantially uniform, irrespective of direction in which specimens were taken. Even though Young's modulus of brand 19 is high, the extensibility compares favorably with that of the other brands of dry-press brick. Brand 20, a chrome brick, showed exceptional differences in Young's modulus between lengthwise and crosswise specimens, corresponding in this respect to brands 3 and 10. Brand 21, a forsterite brick, on the other hand showed exceptional agreement in Young's modulus as well as strength between lengthwise and crosswise specimens, and in this respect corresponds to brands 8, 11, and 16.

Duplicate sets of nine specimens from three bricks each of brands 2, 6, 7, 8, and 15 were tested and the results are given in table 1. Although values of modulus of elasticity and strength in individual instances show some variation between the original and the duplicate series of test specimens, results in general are satisfactory, especially in view of the inherent variability of firebrick. The mean extensibility (considered the important tensile property from the spalling viewpoint), was in unusually good agreement in each case excepting brand 7, between the first and second lots of bricks tested.

Based on strength and Young's modulus of elasticity of firebrick in tension for the brick sampled both lengthwise and crosswise, the results given in table 1 show that the bricks may be generally classified into the three following types:

1. These properties are approximately alike irrespective of the direction of sampling. Handmade brands are of this type.
2. These properties of the lengthwise specimens are greater than those of the crosswise specimens. The stiff-mud brands are of this type.
3. The moduli of elasticity of the crosswise specimens are greater than of the lengthwise specimens and the strengths are approximately equal. Most of the dry-press brands are of this type.

The results, in general, also show that the dry-press bricks had the greatest extensibility, but that the two handmade brands of highest silica content had outstandingly high extensibilities.

The range in mean extensibilities for the different brands was from 0.0120 to 0.0465 percent, but the great majority of brands were grouped in the comparatively narrow range from 0.0175 to 0.0235 percent. Figure 7 shows the relation of extensibility between lengthwise and crosswise specimens plotted in the order of decreasing extensibility of the lengthwise specimens. The tendency of the crosswise specimens to exhibit a generally lower extensibility than the lengthwise specimen is clearly illustrated.

The coefficient of variation [9] for the lengthwise extensibility of bricks was computed for each brand. The values ranged from 2.2 to 50.2 percent, table 1. When grouped according to method of forming, the mean coefficient for those made by the dry-press process was 13.1 percent, the stiff-mud 16.5 percent, and the handmade 20.4 percent. If brand 12 (badly laminated), which had an exceptional coefficient of variation, is eliminated from the stiff-mud group,

[9] Manual for interpretation of refractory test data. ASTM Standards on Refractory Materials (Feb. 1935). Applying the formulas given to samples of only three bricks, as was done in this study, yielded coefficients of variation which are unduly large.

the value for that group is 11.5 percent. The small sample limits the value of conclusions which may be drawn from these coefficients. They are presented, however, to show the approximate range in variability of some refractory products.

2. EFFECT OF KILN SETTING, LOAD, AND WEIGHT OF BRICK ON TENSILE PROPERTIES [10]

(a) KILN SETTING

The manner of setting bricks in the kiln for the burning operation does not vary materially throughout the industry. The greatest difference enters in the load to which the bricks are subjected because

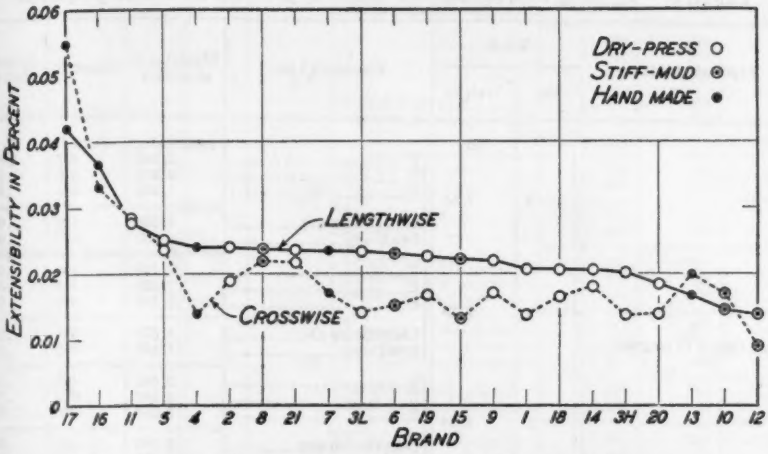

FIGURE 7.—*Graph showing the extensibility of specimens.*

The extensibility of specimens taken parallel to the 9 in. dimension of the br ck (lengthwise) is in most instances significantly greater than that of specimens taken parallel to the 4½ in. dimension (crosswise). The method of forming the brick is also indicated.

of the height of setting. Test results were obtained on one brand for the purpose of comparing the effect on tensile properties of bricks when: (1) set on end, (2) laid flat, and (3) set on edge. Data were obtained on bricks fired when set on end, flat, and on edge, in each case under 13 courses from the top of the setting, and also on bricks fired set on edge on the top course protected from direct heat by a layer of bricks laid flat. The load imposed on the top course of bricks was negligible and the bricks under 13 courses were under an approximate stress of 4.4 lb/in ^{2}. The results are given in table 5. Also included in the table for comparative purposes are data on bricks (brand 3L) fired set on edge but with no information on the height of the course in the kiln from which they were taken. These bricks were furnished at an earlier period by the same manufacturer who supplied the other bricks on which data are given in the table.

A comparison of the bricks burned on end, on edge, and flatwise under the weight of 13 courses shows that those burned on end have a much greater modulus of elasticity and strength lengthwise than crosswise. The average values of all lengthwise specimens for bricks

[10] In this phase of the study the conclusions drawn from the results are of limited value because only one product, one method of manufacture, and a small number of bricks were considered.

set on end give a Young's modulus 70 percent greater and a tensile strength 64 percent greater than the average values of all the crosswise specimens. If values for all specimens, both crosswise and lengthwise, from bricks under 13 courses are averaged according to method of setting, those set endwise showed greater elasticity and strength and lower extensibility than those set either edgewise or flatwise. The data indicate no particular difference in tensile properties between bricks burned edgewise and flatwise, with the exception that the crosswise specimens from bricks set flatwise have a lower modulus of elasticity and greater extensibility than the crosswise specimens from bricks set either edgewise or endwise.[11]

TABLE 5.—*Effect of kiln setting and weight of firebrick on tensile properties*

Method of setting	Brick		Specimen [1] no.	Modulus of elasticity	Strength	Extensibility
	No.	Weight				
		lb		1,000 lb/in.[2]	lb/in.[2]	%
End, under 13 courses	2	7.55	T	2,240	400	0.0180
			B	2,270	440	.0195
			E	1,280	275	.0215
			Lengthwise avg	2,255	420	.0185
			Brick avg	1,930	370	.0195
	4	7.59	T	1,735	380	.0220
			B	1,420	315	.0220
			E	1,160	240	.0205
			Lengthwise avg	1,575	345	.0220
			Brick avg	1,440	310	.0215
	3	7.65	T	2,480	480	.0195
			B	2,480	490	.0200
			E	1,260	250	.0200
			Lengthwise avg	2,480	485	.0195
			Brick avg	2,075	410	.0200
			Lengthwise avg	2,105	420	.0200
			Crosswise avg	1,235	255	.0205
			Setting avg	1,815	365	.0205
Edge, under 13 courses	5	7.54	T	1,430	335	.0235
			B	1,370	330	.0240
			E	1,190	250	.0210
			Lengthwise avg	1,400	330	.0235
			Brick avg	1,330	305	.0230
	3	7.55	T	1,590	360	.0225
			B	1,410	315	.0225
			E	1,600	295	.0185
			Lengthwise avg	1,500	335	.0225
			Brick avg	1,535	320	.0210
			Lengthwise avg	1,450	335	.0230
			Crosswise avg	1,395	270	.0195
			Setting avg	1,430	315	.0230
Edge (3L)[3] height of setting unknown.	1		T	1,730	395	.0230
			B	1,650	390	.0225
			E	2,550	350	.0140
	2		T	1,820	425	.0225
			B	1,590	365	.0230
			E	2,690	340	.0125
	3		T	1,100	270	.0245
			B	1,280	285	.0225
			E	2,350	365	.0155

[1] Refers only to brand 3, made by the dry-press method of forming.
[2] Sampled in accordance with method illustrated in figure 1, also figure 6 (brick III).
[3] Refers to brand 3L.

[11] It may be concluded that bricks set flatwise during firing should prove superior in installations of header construction where thermal spalling is an important consideration.

TABLE 5.—*Effect of kiln setting and weight of firebrick on tensile properties*—Con.

Method of setting	Brick No.	Brick Weight	Specimen no.	Modulus of elasticity	Strength	Extensibility
		lb		1,000 lb/in.	lb/in.	%
Edge (3L) height of setting unknown.			Lengthwise avg	1,530	355	.0235
			Crosswise avg	2,530	350	.0140
			Setting avg	1,860	355	.0200
Flat, under 13 courses	4	7.29	T	1,375	300	.0215
			B	1,250	280	.0225
			E	855	210	.0245
			Lengthwise avg	1,315	290	.0220
			Brick avg	1,160	265	.0230
	5	7.54	T	1,100	245	.0220
			B	1,040	265	.0255
			E	920	235	.0260
			Lengthwise avg	1,070	255	.0240
			Brick avg	1,020	250	.0245
	2	7.58	T	1,750	435	.0250
			B	1,700	410	.0240
			E	1,530	315	.0205
			Lengthwise avg	1,725	420	.0245
			Brick avg	1,660	385	.0230
			Lengthwise avg	1,370	320	.0235
			Crosswise avg	1,100	255	.0235
			Setting avg	1,280	300	.0235
Edge, under 1 course	4	7.52	T	1,845	390	.0210
			B	1,280	265	.0210
			E	1,360	255	.0185
			Lenthwise avg	1,560	320	.0210
			Brick avg	1,495	305	.0200
	2	7.56	T	2,040	355	.0175
			B	1,925	420	.0215
			E	1,540	335	.0215
			Lengthwise avg	1,980	385	.0195
			Brick avg	1,835	370	.0200
	5	7.66	T	2,635	485	.0185
			B	2,185	420	.0195
			E	2,280	505	.0220
			Lengthwise avg	2,415	450	.0190
			Brick avg	2,370	470	.0200
			Lengthwise avg	1,985	390	.0200
			Crosswise avg	1,725	365	.0210
			Setting avg	1,900	380	.0200

(b) LOAD

Whether specimens during firing were subjected to axial or lateral load depended on the method of setting in the kiln. In figure 8 bars representing tensile properties are designated H and V to indicate which specimens were in a horizontal position under lateral load, and those in a vertical position under axial load during heating, irrespective of the setting or position of the brick. Horizontal-shading lines within the bars refer to specimens taken crosswise and vertical-shading lines to specimens taken lengthwise of the brick. Table 5 gives the actual values for the tensile properties of these specimens. This table and figure 8 show that the tensile properties are significantly affected by axial load. It is probable that the properties were

also affected somewhat by lateral load, although no data are available to evaluate this effect.

In studying the effects of load on the tensile properties of the specimens, the *differences* in properties between crosswise specimens

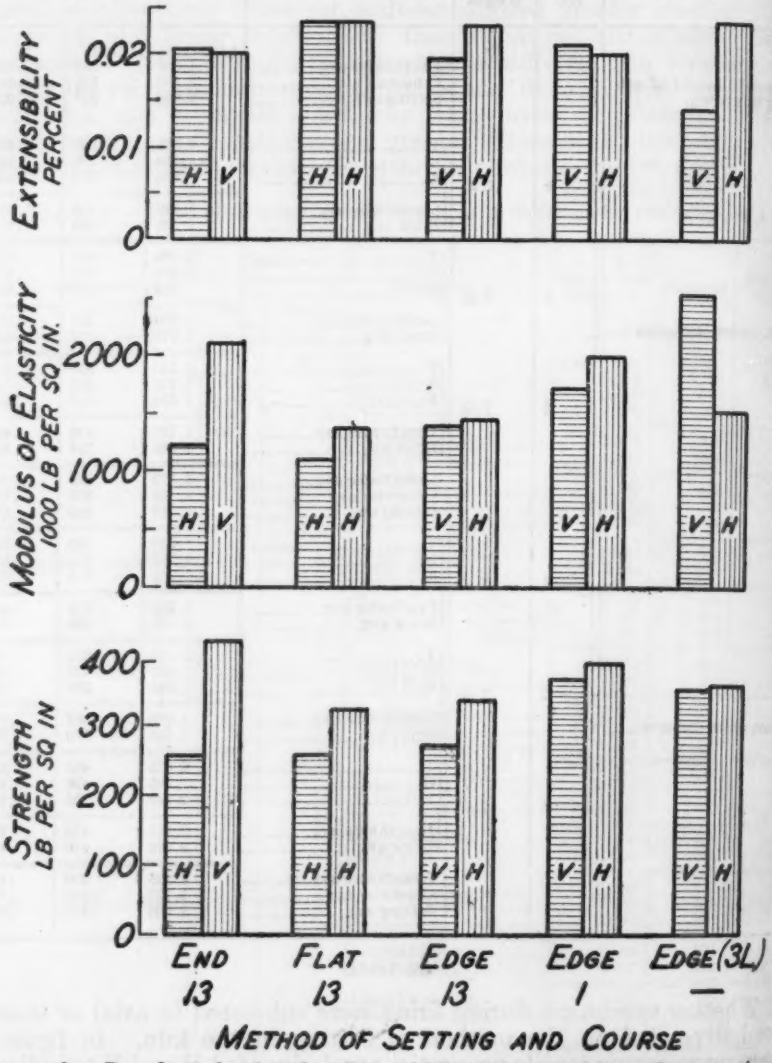

FIGURE 8.—*Bar chart showing the effects of kiln setting on the tensile properties of bricks.*

The bars made up of shading lines parallel to the base represent data on specimens taken crosswise to the brick whereas those made up of lines vertical to the base represent specimens taken lengthwise. The markings H and V indicate that axes of specimens during firing were horizontal or vertical, respectively.

and lengthwise specimens for any one method of setting were compared with these differences for other methods of setting. The difference in modulus of elasticity between vertical V and horizontal H specimens for the edge 1 setting is about the same as that between the crosswise and lengthwise specimens of the flat 13 setting (all speci-

mens in horizontal H position) even though the mean modulus of elasticity of the edge 1 specimens is considerably greater than that of the flat 13 specimens. As far as axial loading of the specimens is concerned, both settings would be considered as under no load. However, when axial load is applied the modulus of elasticity of the vertical V specimens is increased relative to that of the horizontal specimens. This is especially apparent when the difference in modulus of elasticity between the H and V specimens from the bricks in the edge 1 setting is compared with that of the H and V specimens taken from bricks in the edge 13, end 13, and edge (3L) settings. The difference in height of the bars for the edge 1 specimens has been almost eliminated in the edge 13 specimens, and has actually been reversed in the end 13 and edge (3L) [12] specimens.

It may be noted further that the effect of axial load in the end 13 setting is similar to that in the edge (3L) setting, although in the first case the lengthwise specimens were under axial load, and in the second case the crosswise specimens were under axial load.

There is some tendency for the strength of the vertical, V, or axially loaded specimens to increase relative to that of the horizontal, H. The general effect of load on the extensibility is for that of the vertical specimens to be decreased relative to that of the horizontal specimens.

In analyzing these data the effect of heat treatment was not considered, but its effect may be observed by comparing, for example, the lengthwise average values of the properties (table 5) for bricks set edgewise under the weight of 13 courses with those for bricks set edgewise in the top course. It is probable that most of the difference in these average values was due to difference in heat treatment,[13] although it is probable also that the difference in lateral load had some effect.

(c) WEIGHT OF BRICK

Table 5 gives the weights of the 11 dry-pressed bricks included in the study of the effects of method of kiln setting on tensile properties. The weights ranged from 7.29 to 7.66 lb. The relation between weight and modulus of elasticity was determined for each method of setting. In 9 out of 11 cases the Young's modulus increased with weight.[14] However, because of the small number of samples, the value of a quantitative evaluation of the relation would be limited, and this relation might not apply to either the stiff-mud or the handmade process of manufacture.

VI. SUMMARY AND CONCLUSIONS

The tensile properties of 22 different brands of firebrick at room temperature were determined. The chemical composition, porosity, pyrometric-cone equivalent, and method of manufacture for most of the materials are included.

A testing machine of the simple lever type, especially constructed for the study, is described. Deformation measurements were

[12] The data lead to the conclusion, without any consideration for degree of temperature, that bricks edge (3L) were loaded under considerably more than 13 courses during kiln firing.

[13] R. A. Heindl and W. L. Pendergast, BS J. Research **3**, 691 (1929) RP114.

[14] In forming dry-pressed bricks, the quantity of material filling the mold boxes varies, but the bulk volume of the resulting bricks is substantially the same and the difference in weight is, therefore, due to difference in quantity of material filling the mold box. The bulk volume of the bricks was not determined.

obtained with the Tuckerman optical strain gage, which permitted readings to be duplicated to within 0.000002 in.

Three different methods of obtaining specimens from the individual brick were tried, and the results of tests on selected specimens are given. In the method adopted, three specimens were machined from each brick, two lengthwise and one crosswise of the brick. The lengthwise specimens provided a 3-in. gage length and the crosswise a 2-in. gage length. All specimens had a cross-sectional area of 1.50 sq in. in the gage length.

The following results were obtained:

1. Based on strength and Young's modulus of elasticity of firebrick in tension, for the brick sampled both lengthwise and crosswise, the bricks may be generally classified into three types as follows: (*a*) These properties are approximately alike irrespective of the direction of sampling—handmade bricks were of this type; (*b*) these properties of lengthwise specimens are greater than those of the crosswise specimens—the stiff-mud bricks were of this type; and (*c*) the modulus of elasticity of the crosswise specimens is greater than that of the lengthwise specimens and the strengths are approximately equal—most of the dry-pressed bricks were of this type.

2. The range in extensibilities for all brands of bricks is from 0.0120 to 0.0465 percent, but the majority of firebricks are grouped within the comparatively narrow range from 0.0175 to 0.0235 percent. A highly siliceous fire-clay brick and a silica brick, with higher silica content than the other brands and both formed by the handmade process, had extensibilities much greater than the other brands.

3. In general, bricks formed by the dry-press process had greater extensibilities than those formed by either the handmade or the stiff-mud process.

4. When comparing the tensile properties of several bricks of the same brand, handmade bricks were more variable from one brick to the next than either stiff-mud or dry-pressed bricks. However, the range from maximum to minimum values for individual bricks is less for the handmade bricks than for either of the other types.

5. From the limited data obtained on bricks fired under no load, when compared with those fired under a load of 13 courses (stress approximately 4.4 lb/in.^{2}), it was noted that the tensile properties of the specimens subsequently cut from the bricks were significantly affected by axial load during heating. It is probable that the properties were also affected somewhat by lateral load, although no data were obtained to evaluate this effect. In those bricks fired under a load of 13 courses the difference in the modulus of elasticity and in the strength lengthwise and crosswise was greater in the bricks burned on end than in those set edgewise or flatwise. Of the three methods, the end setting had also the highest modulus of elasticity and strength and the lowest average extensibility.

In general, the modulus of elasticity of dry-pressed bricks increased with the weight of the brick.

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IONIZATION OF AIR BY LENARD RAYS

By Lauriston S. Taylor

ABSTRACT

Lenard rays in atmospheric air have been measured by means of simple ionization chambers. At ordinary intensities, encountered with Lenard rays, it is impossible to saturate such ionization chambers and this has resulted in neglect of the method for practical purposes. It has been found, however, that plotting the reciprocal current against the reciprocal voltage, a straight line results, which can be extrapolated to $1/V=0$; thereby giving the current at infinite field. A number of such cases are given. Unipolar conductivity is evident in at least one ionization chamber.

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I. INTRODUCTION

In 1930 a study was undertaken to arrive at a reliable method for measuring Lenard rays in such applications as the activation of ergosterol and the study of cathode ray biological effects.[1]

By intensity of Lenard rays is meant the rate of passage of electrons across unit area normal to the beam.[2] This does not involve the velocity distribution of the electrons within the beam. After investigating several, it was decided that the most direct method of measuring Lenard ray intensities was probably that employing a faraday collector.[3]

On the other hand, the measurement of Lenard rays with an ionization chamber involves problems analogous to those commonly encountered in the measurement of X-rays and has the important advantage of being more simply related to the absorption in biological media. The ionization current is proportional to the fractional part of the energy of the whole beam, which is absorbed in the measuring volume of the chamber. This in turn depends upon the quality or velocity distribution of the electrons—a quantity which, at best, can only be expressed in terms of some average distribution or composite absorption coefficient.[4]

[1] This work was discontinued in 1932, and since the apparatus has largely been disassembled, it is not feasible at present to investigate further some of the problems suggested by a study of the old data.
[2] L. S. Taylor, Radiology **12**, 294 (1929).
[3] L. S. Taylor, BS J. Research **7**, 57 (1931) RP332.
[4] L. S. Taylor, BS J. Research **12**, 401 (1934) RP666; Radiology **22**, 445 (1934).

In addition, the air ionization method of measurement offers a convenient mode of control and is presumably proportional to the intensity of a given quality. The use of a simple ionization chamber was tried, but it was abandoned because of inability to reach saturation without causing a disruptive breakdown of the air by collision ionization under the high electrostatic fields employed.

Recent studies [5] have led to an application of Jaffe's theory of columnar ionization,[6] whereby it is possible to derive the saturation current value in liquids exposed to X-rays. Clay and Van Tijn [7] and Zanstra [8] have independently arrived at similar results in the case of high-pressure gaseous ionization chambers exposed to gamma

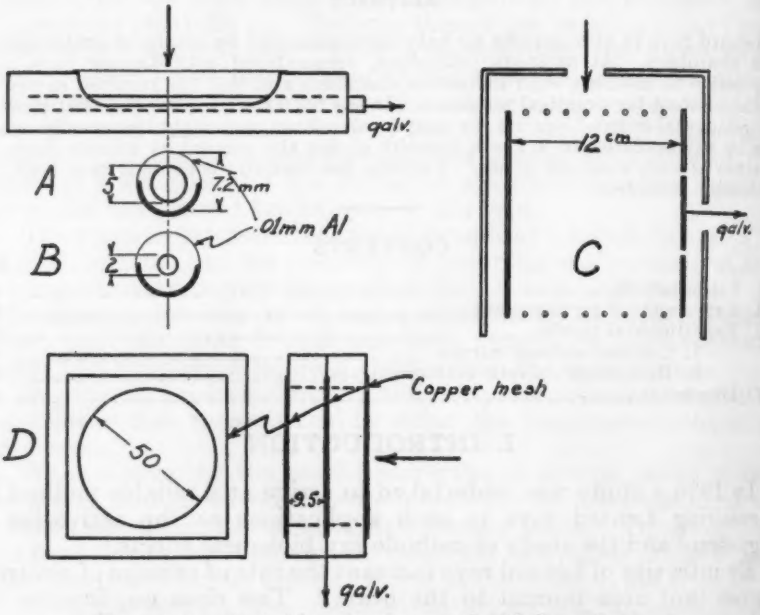

FIGURE 1.—*Ionization chambers used with Lenard rays.*

rays. These studies have led us to investigate the shape of the saturation curves produced by Lenard rays in air at normal pressure.

II. EXPERIMENTAL ARRANGEMENT

The detailed description of the apparatus has been given in an earlier paper.[9] The cathode rays were produced in a sealed-off Lenard tube with a thin glass window, designed by Slack [10] and operated from a high-voltage source of the Villard rectifier type. The voltage was approximately a sine wave above ground with a peak value of 150 kv. Input voltage was supplied by a synchronous motor-generator set and hence reasonably steady. Output voltage was controlled and measured directly with a high-resistance voltmeter. Tube current, measured between anode and ground, was maintained at 21×10^{-6} amp.

[5] F. L. Mohler and L. S. Taylor, BS J. Research **13**, 659 (1934) RP733.
[6] G. Jaffe, Ann. Phys. **42**, 303 (1913).
[7] J. Clay and M. A. Van Tijn, Physica **2**, 825 (1935).
[8] H. Zanstra, Physica **2**, 817 (1935).
[9] L. S. Taylor, BS J. Research **7**, 57 (1931) RP332.
[10] C. M. Slack, J. Opt. Soc. Am. **15**, 123 (1929).

The ionization chamber was mounted on a track in front of the tube window. The ionization current (10^{-7} to 10^{-8} amp) was measured with a galvanometer connected between the chamber and tube anode. One set of measurements for currents of about 10^{-10} amp was made with a capacitance compensator and electrometer.[11]

Ionization chambers (fig. 1) of the following descriptions were used: A, cylinder, brass tube 7.2 mm inside diameter, cut away for about half its circumference and covered with 0.01 mm of Al; collector rod 5 mm diameter; opening length 5 cm. B, same as for A, except collector rod was 2 mm diameter. C, parallel plate, guarded-field ionization chamber [12] with snout and back removed. D, parallel copper mesh (32), 1 cm spacing, 5 cm diameter. E, cylinder copper mesh (32), 8 mm inside diameter, collector 2 mm diameter. Chamber A was used with three different Lenard ray qualities, distinguished by A_1, A_2, and A_3 in the text and plots.

The Lenard ray beam was limited in cross section by a thin metal diaphragm placed in front of the tube window. This diaphragm had a diameter of 14 mm, with A, B, and E, 2.9 mm with C, and 1.9 mm with D.

III. EXPERIMENTAL RESULTS

1. CURRENT-VOLTAGE CURVES

Curves for the ionization current as a function of the applied voltage are given in figure 2 for chambers A to D. Applied voltage rather than field strength is used as abscissas since the latter is indeterminate. It is seen in the case of curves A_1, A_2 and A_3, that noticeable collision ionization begins at about 1,000 volts, which corresponds roughly to a field strength of about 9 kv/cm. In all other cases, this high field strength was not approached, and no evidence of collision ionization was noted.

It is also to be noted that at high field strengths, saturation is nearly reached, whereas for the very low fields used in parallel-plate chamber C there is no apparent evidence of approach to saturation.

It was not possible to vary the degree of the ionization by a known amount without at the same time introducing other variables, such as electron diffusion and change in velocity distribution. Hence, there is no simple direct way to ascertain whether or not the ionization current below saturation is proportional to the radiation intensity. This was attempted by indirect means. Previous studies have indicated the reliability of a faraday collector for measuring the Lenard current.[9] The intensity of the beam was therefore varied by filtering with thin aluminum foil, and absorption curves of the resultant radiation obtained first with the faraday chamber and then with ionization chamber A at 900 volts, which is probably within 10 percent of saturation. This was done for three different distances, d, between the tube window and faraday collector or ionization chamber.

Figure 3 shows the results, where curves M are for the ionization chamber and curves N are for the ratio R of the ionization current to the faraday current. On the assumption that the measurements by

[11] L. S. Taylor, BS J. Research **6**, 807 (1931) RP306.
[12] L. S. Taylor and G. Singer, BS J. Research **5**, 507 (1930) RP211.

the faraday chamber are correct, the relative sensitivity of the ionization chamber changes rapidly, increasing as the ionization becomes weaker.

An explanation for the apparently great disparity between the measurements by the two methods probably lies in the fact that whereas the faraday collector measures the total Lenard current, the ionization current gives only a measure of the fraction of the energy of the electrons absorbed within the ionization chamber. With no filter, fast cathode rays with low ionizing power pass completely

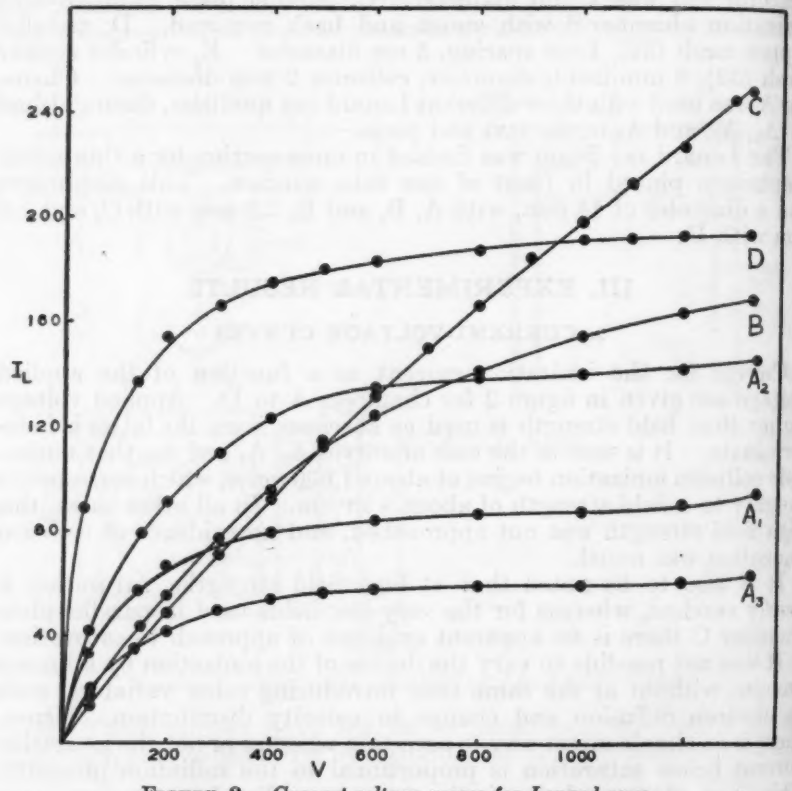

FIGURE 2.—*Current-voltage curves for Lenard rays.*

through the chamber. With increase in filtration an increasing fraction of the electrons terminate their paths within the chamber. and thereby produce a greater amount of ionization in accordance with Bragg's findings in terminal ionization.

2. RECIPROCAL CURRENT-VOLTAGE CURVES

Suggested by the results of plotting the reciprocal current against reciprocal voltage in the case of liquids (Mohler and Taylor) and high-pressure gases (Zanstra), the above data were similarly treated on purely empirical grounds.[13] Such a plot compresses the scale at the upper voltages so that an extrapolation to infinite fields is rendered practical.

[13] L. S. Taylor, Phys. Rev. 48, 970 (1935).

The data of figure 2 were accordingly plotted with the reciprocal current against the reciprocal voltage in figures 4 and 5. It is seen that even down to comparatively low field strengths there is a linear relationship between the two quantities. In the case of chamber A, the field strength of 9.0 kv/cm gave very nearly the saturation current, as shown in figure 2. It would appear safe, therefore, to extrapolate the curve to $1/V=0$, thereby deriving a magnitude for the ionization current I_∞ at infinite field.

Similarly the other curves are extrapolated to $1/V=0$, since they are straight lines even in the extreme case of chamber C where the maximum field strength was about 0.15 kv/cm. Table 1 gives a summary of the experimental factors and also the ratio I_0/I_∞ of the highest measured current, I_0, to the derived maximum I_∞.

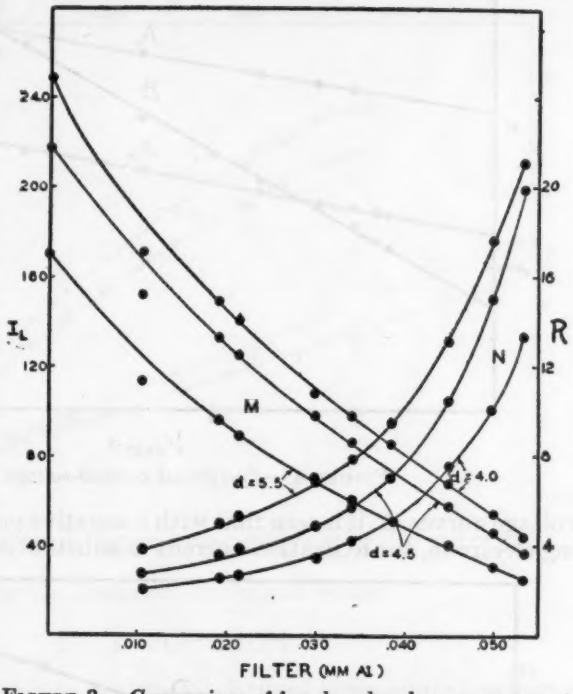

FIGURE 3.—*Comparison of faraday chamber measurement and ionization measurement of Lenard ray.*

With the exception of chambers C and D, the field strengths given do not have great significance—especially those marked with an asterisk—since in all cases, the field is radial and hence not uniform. In chambers A_1, A_2, and A_3 the radii of the inner and outer cylinders are 2.5 and 3.6 mm, respectively, so the field is considerably more uniform than in chambers B and E.

TABLE 1.—*Lenard ray intensities.*

Chamber	Tube distance[1]	Tube diameter	Filter	Maximum field strength	I_∞	$\frac{I_0}{I_\infty}$
	Centimeter	Millimeter	Millimeter	kv/cm	amp×10⁻⁶	
A_1	7.3	14	----------	9.1	17.1	0.91
A_2	4.6	14	----------	9.1	53.8	.86
A_3	4.6	14	0.2 Al	9.1	21.6	.93
B	4.6	14	----------	*3.2	91.2	.51
C	----------	2.9	----------	.13	29.3	.28
D	6.6	.9	----------	1.4	6.65	.90
E_2	4.6	14	----------	*2.5	77.8	.35
E_4	4.6	14	----------	*2.5	77.8	.35

[1] Airpath between tube window and ionization chamber.
* See explanatory text above.

The effect of reversing the potential on the chamber is shown in figure 6 for the cylindrical chamber E. From the simple current-

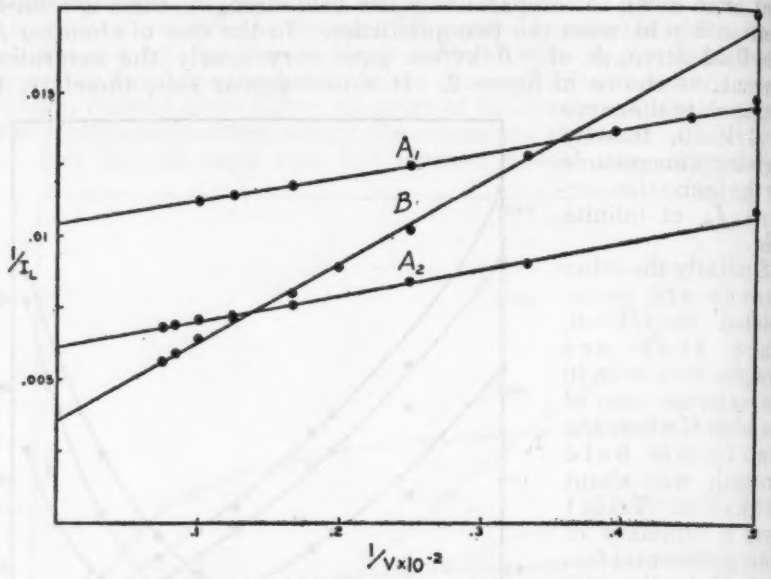

FIGURE 4.—*Reciprocal current-voltage curves*

voltage curves, A, it is seen that with a negative potential on the collecting electrode, the ionization current is substantially larger than when

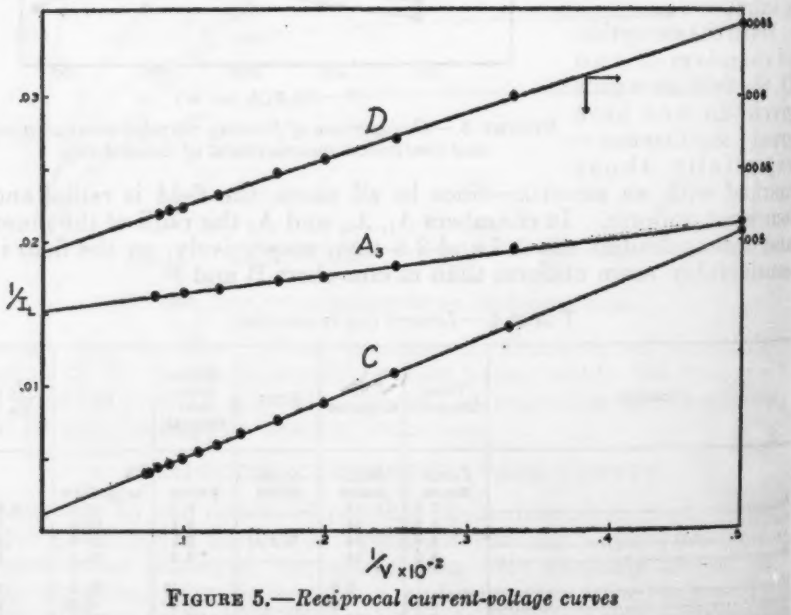

FIGURE 5.—*Reciprocal current-voltage curves*

it is positive. Curves b show the same data plotted reciprocally; it is seen that although the points fall on two distinct straight lines, they extrapolate to the same value of $1/I$, for $1/V=0$.

Included in table 1 are the values of I_∞, which may be used for rough calculations of the ionization per unit volume, absolute values of which cannot be obtained for lack of sufficient definition of the beam and ionized volume. The effective volumes of chambers A_2 and B are roughly in the ratio of 1:2, with which the respective values of I_∞ agree.

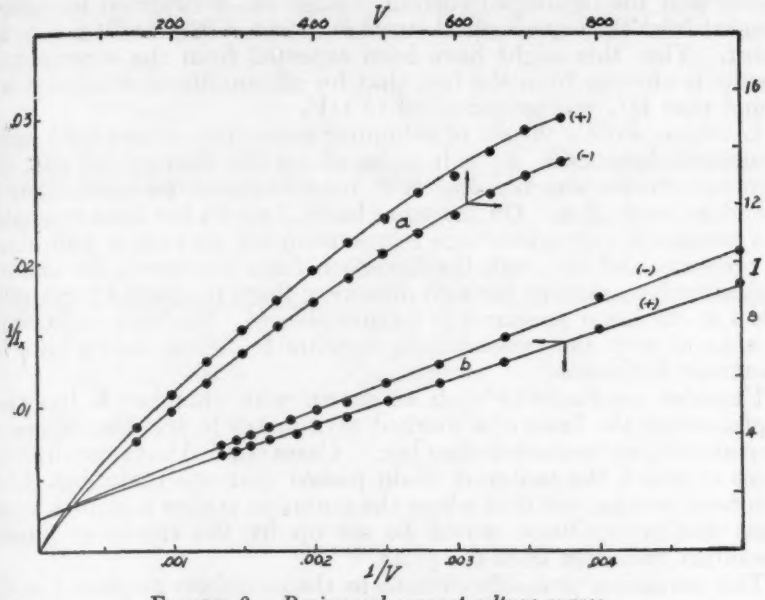

FIGURE 6.—*Reciprocal current-voltage curves.*

IV. DISCUSSION

An attempt was made to explain the form of these ionization curves on the basis of some existing theory, but this is rendered too complicated by the inhomogeneous electric field in all chambers but C and D. The relationship between ionization current and field strength for a uniformly ionized chamber has been found by others to agree fairly well with the theories of Thomson,[14] Nice, and Seemann for X-rays and β rays of moderate intensity (up to 5 roentgens per minute, for X-rays). However, the intensities involved here are of the order of 1,000 times as large, and hence initial and intercolumnar recombination may be of greater importance here than in the cases of low ionization densities.

Thomson's equation for the ionization current I_x at a given field strength X, where I_x is small compared with I_∞, is

$$\frac{I^2_x}{I_\infty - I_x} = \frac{(k_1+k_2)^2 X^2}{\alpha/e.l},$$

where l is the plate separation, α the recombination coefficient, and e the charge on the electron. Taking the square root of both sides of this equation it is seen (curve C, fig. 2) that for small values of I_x there is a nearly linear relation between I_x and X. The conditions in the equation may be approximately fulfilled by the chamber C and

[14] See J. J. Thomson, Conduction of Electricity Through Gases (Cambridge, 1928).

possibly E where the ratios I_x/I_∞ were 0.28 and 0.35, respectively. It is, indeed, true that the curves are linear for these chambers, but it is equally true that they are linear for the other chambers where I_x/I_∞ is 0.9, a magnitude too large for fulfilling the conditions of approximations. Assuming that this relation holds for the maximum ionization current measured with parallel-mesh chamber D, it was found that the calculated current-voltage curve deviated by several percent from the experimental curve even at the 98 percent saturation point. That this might have been expected from the experimental results is obvious from the fact that for all conditions studied it was found that $1/I_x$ was proportional to $1/V$.

Likewise, Jaffé's theory of columnar ionization cannot hold under conditions here used, since it is based on the assumption that the columns do not overlap and that intercolumnar recombination is, therefore, negligible. On the other hand, Zanstra has been evaluated the ionization current-voltage relationship for air over a wide range of pressure, and although the deviation from the curves for uniform ionization is marked at the high pressures, there is a barely perceptible effect at the lower pressures (8.8 atmospheres). We have no explanation as to why the present data appears to follow Jaffé's laws for columnar ionization.

Unipolar conductivity such as shown with chamber E has been explained on the basis of a marked asymmetry in the distribution of ionization in an ionization chamber.[15] Cases studied have usually been those in which the radiation beam passed near one plate, but it has also been pointed out that where the radiation strikes a plate, a somewhat similar condition would be set up by the relatively intense secondary radiation from the plate.

This condition probably obtains in the chambers employed in the present work. In addition, since the Lenard rays are absorbed strongly by air, the ionization density will be substantially less at the emergent side than at the entrance side of the chamber. Of particular interest, however, is the fact that regardless of the sign of the potential on the plates, the relationship of $1/I_x$ to $1/X$ is linear at high field strengths. Moreover, under the same radiation conditions both curves extrapolate to identically the same value of $1/I_x$ for $1/X=0$. This latter fact would seem to definitely indicate the validity of a reciprocal current-voltage relationship and the permissibility of obtaining the true saturation current by extrapolation. For it is reasonable to expect the actual number of ions formed to be independent of any potential applied to the plates (except above the field strength where collision ionization occurs) and hence yield the same saturation current under conditions where no ions are lost by recombination.

The difference in ionization current at the lower fields might also be caused by electric field inhomogeneity, but it is interesting to note that exactly similar curves have been reported by Clay and Van Tijn [16] for a parallel-plate chamber with air under high pressure and using gamma rays as the ionizing agent. We have also found similar results for parallel-plate air ionization chambers with very intense X-rays.[17]

WASHINGTON, July 1, 1936.

[15] E. Rutherford, Phil. Mag. [VI] 2, 210 (1901).
[16] F. L. Mohler and L. S. Taylor. BS J. Research 13, 659 (1934) RP733.
[17] Data to be published later.